

INSTITUTE OF METALS
DIVISION

1944

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N/C **TRANSACTIONS**

OF THE

**AMERICAN INSTITUTE OF MINING
AND METALLURGICAL ENGINEERS**

(INCORPORATED)

and Petroleum

Volume 156

INSTITUTE OF METALS DIVISION
1944

TECHNICAL PAPERS, DISCUSSIONS AND A SYMPOSIUM PRESENTED
BEFORE THE DIVISION AT MEETINGS HELD AT CHICAGO,
OCTOBER 16-20, 1943, AND NEW YORK, FEBRUARY 20-24, 1944

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Notice

This volume is the eighteenth of a series constituting the official proceedings of the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers. It deals with nonferrous metals and includes papers presented at the Chicago Meeting, Oct. 16-20, 1943, and the New York Meeting, Feb. 20-24, 1944. The complete list of publications and proceedings, including the present volume, is as follows:

1908-1911 *Transactions* of the American Brass Founders' Association: 1908, Vols. 1 and 2; 1909, Vol. 3; 1910, Vol. 4; 1911, Vol. 5.

1912-1916 *Transactions* of the American Institute of Metals, Vols. 6-10.

1917-1918 *Journal* of the American Institute of Metals, Vols. 11-12.

1919-1926 *TRANSACTIONS* of the American Institute of Mining and Metallurgical Engineers, Volumes 60, 64, 67, 68, 69, 70, 71 and 73.

1927-1928 *PROCEEDINGS* of the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers, two volumes, of which the later is now designated Vol. 78 of the A.I.M.E. *TRANSACTIONS*.

1929-1943 *TRANSACTIONS* of the American Institute of Mining and Metallurgical Engineers, Volumes 83, 89, 93, 99, 104, 111, 117, 122, 124, 128, 133, 137, 143, 147, 152 and 156, Institute of Metals Division.

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FOREWORD

The members of the American Institute of Mining and Metallurgical Engineers interested in physical metallurgy or in the structure and properties of nonferrous alloys have every reason to be proud of the 1944 volume of the TRANSACTIONS recording the proceedings of the Institute of Metals Division. It is safe to say that nearly all of the members of our Division are in one way or another subject to the great pressure connected with the extremely high production of nonferrous metals for war purposes, but despite this, the current volume is outstanding, not only in the high quality of the papers, but also in the number of papers and in the diversified fields they cover.

Considering the fact that this volume contains no papers on nonferrous smelting and refining, it is the largest in years, and it is fitting that I take this opportunity to express my appreciation here for the splendid work done by the Division's Programs Committee, under the chairmanship of E. A. Anderson, and the Division's Publications Committee, under the chairmanship of E. E. Schumacher, in arranging the program for the Annual Meeting in New York City and the Fall Meeting in Chicago, and in maintaining the high quality that is always associated with the papers of our group.

In addition to the usual quota of reports of research on copper and copper-rich alloys and six other interesting papers on structure and properties, the volume includes five papers on what might be termed pure physical metallurgy, of which two are important contributions to our knowledge of the electron microscope. Special attention is also directed to this year's Institute of Metals Division lecture, on "Some Problems in Organizing Industrial Research," by W. M. Peirce. This is a broad discussion of research as organized and carried out by a large metal producer and can be read with much profit by all metallurgists and executives in the metal-producing and metal-using industries.

The volume also contains a number of papers on diffusion—the first of a series of comprehensive symposia. Although a paper prepared especially for a symposium cannot usually be called a report of research, such papers are a relatively broad survey of a particular field and the Division's Publications Committee in considering this symposium felt that it should be included in this volume. There is a large segment of the membership of our Division that is interested primarily in so-called "practical" metallurgy and because of this, E. A. Anderson, Chairman of the Programs Committee, has outlined a long-term program of symposia, which, it is felt, will round out the service our Division gives to its members and to the nonferrous industries at large. The symposium included in this volume is only the first of a series and the Executive Committee of the Division feels confident that it will prove of much interest and of lasting value to a considerable proportion of our membership.

ARTHUR PHILLIPS, *Chairman,*
Institute of Metals Division.

NEW HAVEN, CONNECTICUT

August 1, 1944.

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BYLAWS OF THE INSTITUTE OF METALS DIVISION

(As approved by the Board of Directors September 16, 1937; Art. VII, Sec. 7, approved March 17, 1939; Art. V, Secs. 1, 3, and 4, and Art. 7, Sec. 1, approved June 21, 1944)

ARTICLE I

NAME AND OBJECT

SEC. 1. This Division shall be known as the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers.

SEC. 2. The object of the Division shall be to furnish a medium of cooperation between those interested in the metallurgy, fabrication and uses of the nonferrous metals and their alloys; to represent the A.I.M.E. in so far as nonferrous metallurgy is concerned, within the rights given in A.I.M.E. Bylaw XI., Sec. 1, and not inconsistent with the Constitution and Bylaws of the A.I.M.E.; to hold meetings for social intercourse and the discussion of nonferrous metallurgy; to stimulate the writing, presentation and discussion of papers of high quality on nonferrous metallurgy; to reject or accept such papers for presentation before meetings of the Division.

ARTICLE II

MEMBERS

SEC. 1. Any member of the A.I.M.E. of any class and in good standing may become a member of this Division upon registering in writing a desire to do so, but without additional dues.

SEC. 2. Any member not in good standing in the A.I.M.E. shall forfeit his privileges in the Division.

ARTICLE III

FUNDS

SEC. 1. The expenditure of the funds received by the Division shall be authorized by the Executive Committee of the Division.

ARTICLE IV

MEETINGS

SEC. 1. The Division shall meet at the same time and place as the Annual Meeting of the A.I.M.E., and at such other times and places as may be determined by the Executive Committee subject to the approval of the Board of Directors of the A.I.M.E.

SEC. 2. The annual business meeting shall be held within a few days before or after the annual business meeting of the A.I.M.E.

SEC. 3. At any meeting of the Division for which notice has been sent to the members of the Division through the regular mail at least one month in advance, a business meeting may be convened by order of the Executive Committee, and any routine business transacted not inconsistent with these Bylaws or with the Constitution or Bylaws of the A.I.M.E.

SEC. 4. For the transaction of business, the presence of a quorum of not less than 25 members of the Division shall be necessary.

ARTICLE V

OFFICERS AND GOVERNMENT

SEC. 1. The officers of the Division shall consist of a Chairman, a Senior Vice-chairman, one Vice-chairman, Secretary and Treasurer. The office of Secretary and Treasurer may be combined in one person, if desired by the Executive Committee.

SEC. 2. The government of the affairs of the Division shall rest in an Executive Committee, in so far as is consistent with the Bylaws of the Division and the Constitution and Bylaws of the A.I.M.E.

SEC. 3. The Executive Committee shall consist of the Chairman, Senior Vice-chairman, Vice-chairman, past Chairman, Secretary, and nine members, all of whom shall be nominated and elected as provided hereafter in Article VII.

SEC. 4. The Chairman, Senior Vice-chairman and Vice-chairman shall serve for one year each, or until their successors are elected. Each member of the Executive Committee shall serve three years. The Chairman shall remain a voting member of the Executive Committee for one year after his term as Chairman.

SEC. 5. The Treasurer of the Division shall be invited to meet with the Executive Committee, but without ex-officio right to vote. He shall be appointed annually by the Executive Committee, from the membership of the Executive Committee or otherwise.

SEC. 6. The annual term of office for officers of the Division shall start at the close of the Annual Meeting of the Institute and shall terminate at the close of the next Annual Meeting.

ARTICLE VI

COMMITTEES

SEC. 1. There shall be six standing committees as follows: Papers and Programs Committee, Finance Committee, Data Sheet Committee, Membership Committee, Annual Lecture Committee and Annual Award Committee and such other Committees as the Executive Committee may authorize.

SEC. 2. It shall be the duty of the Papers and Programs Committee to secure the presentation of papers of appropriate character at meetings of the Division and of the A.I.M.E.

SEC. 3. It shall be the duty of the Finance Committee to inquire into and examine the financial condition of the Division and to consider proper means of increasing its revenue and limiting its expenses. The Finance Committee shall audit the accounts of the Division and report to the Executive Committee prior to the Annual Meeting of the Division. It shall render a budget to the Executive Committee estimating receipts and expenses for the ensuing year so that action can be taken on same at the first meeting following the Annual Meeting.

SEC. 4. It shall be the duty of the Membership Committee to encourage and solicit membership in the A.I.M.E. and in the Division in accordance with the Bylaws and Constitution of the A.I.M.E.

SEC. 5. It shall be the duty of the Annual Lecture Committee to arrange for the presentation at the time of the Annual Meeting of the A.I.M.E. of a lecture on a technical subject of particular interest to the Division and the A.I.M.E. as a whole. This lecture is to be known as the "Institute of Metals Lecture." This Committee shall make all arrangements, financial and otherwise, and render a complete report on same to the Executive Committee.

SEC. 6. The Chairman of the Division shall, subject to approval of the Executive Committee, appoint the Chairman and new members as required of the Committees referred to in Sec. 1.

SEC. 7. Appointments on standing committees shall be for terms of three years each with approximately one-third of the committee membership being appointed each year.

ARTICLE VII

NOMINATIONS AND ELECTIONS OF OFFICERS AND COMMITTEES

SEC. 1. Every year the Division shall elect a Chairman, a Senior Vice chairman, a Vice-chairman, a Secretary and three members of the Executive Committee.

SEC. 2. A Nominating Committee of five members of the Division shall be appointed by the Chairman of the Division subject to the approval of the Executive Committee.

SEC. 3. This Committee shall make its report to the Executive Committee not later than June 1.

SEC. 4. Any ten members of the Division may submit nominations for one or more offices to the Executive Committee not later than August 15, and the persons so nominated shall be included in the official ballot.

SEC. 5. The voting shall be by letter ballot.

SEC. 6. The ballots shall be counted by a committee of tellers appointed by the Executive Committee.

SEC. 7. The Executive Committee shall fill vacancies in any offices of the Division occurring for any reason other than the expiration of term of election.

ARTICLE VIII

AMENDMENTS

SEC. 1. Proposals to amend these Bylaws shall be made in writing to the Executive Committee and signed by at least ten members. They shall be considered by the Executive Committee and announced to the members through the columns of MINING AND METALLURGY, together with any comments or amendments made by the Executive Committee thereon. They shall be voted upon at the annual meeting of the Division in February or by letter ballot, as may be directed by the Executive Committee.

INSTITUTE OF METALS DIVISION

Established as a Division April 26, 1918

(Bylaws published in this volume, pages 7 to 9.)

Officers and Committees for Year ending February 1945

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Treasurer, H. A. MALONEY, New York, N.Y.
Secretary, FRANK T. SISCO, A.I.M.E., 29 W. 39 St., New York 18, N.Y.

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W. M. CORSE, 1918, 1919
W. H. BASSETT, 1920, 1921
W. B. PRICE, 1922, 1923
G. K. ELLIOTT, 1924, 1925
P. D. MERICA, 1926, 1927
S. SKOWRONSKI, 1928, 1929
ZAY JEFFRIES, 1930

SAM TOUR, 1931
C. H. MATHEWSON, 1932
T. S. FULLER, 1933
J. L. CHRISTIE, 1934
W. M. PEIRCE, 1935
E. H. DIX, JR., 1936

A. J. PHILLIPS, 1937
R. F. MEHL, 1938
R. H. LEACH, 1939
EDMUND M. WISE, 1940
D. K. CRAMPTON, 1941
CARL E. SWARTZ, 1942
CYRIL STANLEY SMITH, 1943

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T. A. WRIGHT, New York, N.Y.
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1946
H. L. BURGHOFF, Waterbury, Conn.
GERALD EDMUNDS, Palmerton, Pa.
A. A. SMITH, JR., Barber, N.J.

1947

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GEORGE SACHS

E. H. DIX, JR.

CYRIL STANLEY SMITH

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D. K. CRAWPTON, *Vice-chairman*
W. M. PEIRCE

J. L. CHRISTIE

C. E. SWARTZ

ANNUAL AWARD CERTIFICATE OF THE INSTITUTE OF METALS DIVISION

In 1933, the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers established its annual award of an engraved certificate to the author or authors of the paper that in the opinion of the award committee represents the most notable contribution to metallurgical science among the papers that have been accepted by the Division for presentation at one of its meetings and have been published by the Institute within the three years preceding the date of award. The award is made by the Division each February. There are no restrictions with respect to nationality, age or occupation of the author or authors.

Awards have been made as follows:

- 1934 Robert F. Mehl and Charles S. Barrett: Studies upon the Widmanstätten Structure, I—Introduction. The Aluminum-silver System and the Copper-silicon System. *TRANSACTIONS* (1931) **93**, 78-110.
- 1935 E. A. Anderson, M. L. Fuller, R. L. Wilcox and J. L. Rodda: The High-zinc Region of the Copper-zinc Phase Equilibrium Diagram. *TRANSACTIONS* (1934) **111**, 264-292.
- 1936 Cyril S. Smith and W. Earl Lindlief: A Micrographic Study of the Decomposition of the Beta Phase in the Copper-aluminum System. *TRANSACTIONS* (1933) **104**, 69-105.
- 1937 Arthur Phillips and R. M. Brick: Effect of Quenching Strains on Lattice Parameter and Hardness Values of High-purity Aluminum-copper Alloys. *TRANSACTIONS* (1934) **111**, 94-112.
- 1938 William L. Fink and Dana W. Smith: Age-hardening of Aluminum Alloys, I—Aluminum-copper Alloy. *TRANSACTIONS* (1936) **122**, 284-293.
- 1939 Frederick N. Rhines and Robert F. Mehl: Rates of Diffusion in the Alpha Solid Solutions of Copper. *TRANSACTIONS* (1938) **128**, 185-221.
- 1940 Alden B. Greninger: Martensite Transformation in Beta Copper-aluminum Alloys. *TRANSACTIONS* (1939) **133**, 204-221.
- 1941 S. E. Maddigan and A. I. Blank: Recovery and Recrystallization in Long-time Annealing of 70-30 Brass. *TRANSACTIONS* (1940) **137**, 170-190.
- 1942 F. N. Rhines: A Metallographic Study of Internal Oxidation in the Alpha Solid Solutions of Copper. *TRANSACTIONS* (1940) **137**, 246-288.
- 1943 J. D. Hanawalt, C. E. Nelson and J. A. Peloubet: Corrosion Studies of Magnesium and Its Alloys. *TRANSACTIONS* (1942) **147**, 273-298.
- 1944 A. H. Geisler, C. S. Barrett and R. F. Mehl: Aging in the Solid Solution of Silver in Aluminum. *TRANSACTIONS* (1943) **152**, 182-200.

THE INSTITUTE OF METALS LECTURE

An annual lectureship was established in 1921 by the Institute of Metals Division, which has come to be one of the important functions of the Annual Meeting of the Institute. In 1934 the Division established the custom of presenting a certificate to each lecturer.

A number of distinguished men from this country and abroad have served in this lectureship. The roll is quoted below:

- 1922 Colloid Chemistry and Metallurgy. By Wilder D. Bancroft.
- 1923 Solid Solution. By Walter Rosenhain.
- 1924 The Trend in the Science of Metals. By Zay Jeffries.
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- 1944 Some Problems in Organizing Industrial Research. By W. M. Peirce.

TECHNICAL PAPERS
AND
DISCUSSIONS



W. M. PEIRCE

Institute of Metals Division Lecturer, 1944

Some Problems in Organizing Industrial Research

By W. M. PEIRCE,* MEMBER A.I.M.E.

(Institute of Metals Division Lecture†)

COMMENCING in 1922, each year a lecture has been presented to the Institute of Metals Division at this February meeting. The range of subjects has been very broad. Some speakers have dealt with the most advanced work in the very heart of the science of physical metallurgy. Others have stimulated our imaginations by discussing the most recent progress in related fields of science. Others have told us of the latest art, which is at any moment of greater practical importance than the latest science, of metals. I feel that this broad precedent in the choice of subjects will justify my choosing to talk about some of the prosaic details of how, during the last generation, industry has effectively organized research to accelerate progress in our own and all other fields of science and related art.

A number of years ago I visited one of this country's well-known research laboratories and had the pleasure of chatting for a few minutes with its equally well-known director. Being particularly interested at the time in the organization problems connected with industrial research, I broached that subject. My host stated in effect that he didn't believe in organized research. He was, of course, resorting to a rhetorical hyperbole to point out the danger of overorganization which can so easily drift into regimentation and destroy individual initiative.

Actually nearly all of us, much as we

* Chief of Research Division, Technical Department, The New Jersey Zinc Company (of Pa.), Palmerton, Pennsylvania.

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cherish our personal freedom of action, believe in organization because the history of progress in every field of human activity has been a history of men learning to work together, to cooperate, to create an efficient division of labor. We use organization to achieve this coordination. At the same time our form of organization must not stifle individual initiative or it will prove a deterrent rather than an aid to accomplishment. Research, too, must be organized for greatest achievement but especial skill and care are perhaps needed to avoid stifling the initiative of the individual workers.

I have, of course, followed with keen interest and much benefit the vast amount that has been said and written on this subject in the past twenty years but I still find new stimulation in discussions with my good friends working in this field. It is my hope that this discussion may serve a like purpose.

It would be ungracious not to make due acknowledgment to the many able contributors to this particular phase of human progress, but their very number and the great volume of their writing makes it impossible to trace to any one individual a particular significant and valuable idea. I shall content myself therefore with this general acknowledgment and with acknowledgment of the specific debt that every research man owes to those who have so ably kept before the public, and in particular before industrial executives, the place of research in the modern scheme of things.

Because of the legitimate publicity thus given to research, the day is past when any

question is raised as to the need for industrial research and it is commonly accepted as a necessary item in the budget of a corporation. While twenty years have witnessed a revolution in general attitude in this respect, many problems involved in fitting the research department into its proper place in the industrial organization remain to be clarified and solved. Various, and in some cases radically different, methods of attack on these unsolved problems are still under trial. It is not to be expected that any one system of handling research within a corporation will be found which is best in every set of circumstances, but as we consider the problem of building an effective research organization and making it part of the company as a whole, certain broad simple principles will emerge which it would seem foolish to ignore.

THE PURPOSE OF INDUSTRIAL RESEARCH

First, let us examine the purpose which it is sought to accomplish when a company sets up a research department as a distinct entity. I think that in industry we are rapidly escaping from the misconception of research so clearly pointed out by Willard H. Dow, "Laymen have been trained to think that the physicist or the chemist dives into nature and comes up with something wonderful. That, of course, is not true. The best we can do—indeed the only thing that is worth doing—is, with infinite patience, to work out the laws of nature as they apply to this or that tiny section of matter and then find a way to direct the working of the natural law into a channel where it may serve mankind. That is why the end of every discovery must eventually be a commercial utility."

Thus, the purpose behind a real industrial research department is both to seek new knowledge and to apply it. The mere application of known facts and principles may be excellent electrical or metallurgical or mechanical or chemical engineering but by itself it is not research. It is

equally true that the search for knowledge for its own sake with no attempt to make useful application of it is research but it is not successful industrial research.

We all know that there are hundreds of so-called research laboratories that are merely trouble-shooting organizations to assist either the operating department with manufacturing problems or the sales department with problems of utilization. Now these are necessary functions which must be performed somewhere in the company by very capable personnel. Under certain conditions, these functions may be best performed by the research department, but, if so, they constitute a valuable by-product of research and not research itself. Laboratories constituted solely for this purpose do not fall within the scope of this discussion.

But while it is easy to find laboratories which fail to meet the first criterion of a research laboratory, the search for new knowledge, you would be hard put to name an industrial research laboratory which seeks knowledge but makes no effort to apply it. This is often called pure research. It is rare in industry perhaps not so much for lack of financial support as because most good research men have an urge to see their discoveries put to practical use, a point to which I shall return.

The notion sometimes voiced in the twenties that to seek to make research profitable constituted a prostitution of the scientific spirit has, I think, largely disappeared. At the same time it has become apparent to those in ultimate control of industrial research that the greatest profit may come in the least expected direction and that we must seek knowledge with a faith in its ultimate benefit as well as with the hope of solving specific and immediate problems. It seems hardly necessary to add that no research laboratory can set out to cover the whole field of natural science and that the search for knowledge for its own sake can be directed

into those fields on which the broad interests of a company impinge. Even though such research may be given an initial direction, it cannot be long pursued without leading quite far enough afield to satisfy the most visionary scientist or the most adventurous management.

The first essential to the successful organization of industrial research then, is, that the company understand that the primary function of research is to explore for new knowledge in reasonably delimited fields within the sphere of company interest and to seek practical applications of whatever may be found. They must further realize that while trouble shooting solves problems for other departments, real research creates problems—problems of raw material procurement, manufacturing and sales. Research will not therefore pay dividends unless a spirit of research pervades the whole company and leads to the solution of these problems by the departments involved.

THE PLACE OF THE RESEARCH DEPARTMENT IN THE COMPANY ORGANIZATION

As companies have come to a clear acceptance of this definition of research, it has been reflected in the position of the research department in the organization of the company as a whole. Thus, while it was logical for trouble-shooting laboratories to be part of the operating department and for engineering groups engaged in new design based on old knowledge to be part of engineering, it became clear that a research department engaged in real research should report directly to the president or executive vice president of the company. We now find this the usual practice with the responsible head of the research activities himself a vice president in a rapidly increasing number of cases.

Acceptance of the idea that a research program must include the exploration of new fields without specific objectives in

view carries with it a second important consequence. It is that the research staff must assume the initiative in selecting new fields for investigation. Naturally proposals for major excursions into new territory will be reviewed by the executive to whom the research department reports. There will be a profusion of such proposals and he will aid in selecting those whose potential possibilities seem best suited for integration with the company's general interests. But the research department must be competent to search out suitable new fields for fundamental research and be willing to shoulder the responsibility for investigating them.

Let me hasten to say that there is no intention to imply that ideas for real research work will come only from within the research department. They will come from innumerable sources. Many problems presented by the manufacturing department will require long programs of research for a satisfactory answer and similarly many problems relating to the use of company products will lead to real research. In the balance of this talk, no distinction will be made between problems as to their origin, and problems relating to research on old processes will be considered as subject to the same handling as new process research.

INTERNAL ORGANIZATION

Having defined the primary function of research as the discovery and application of new facts, and having sketched briefly its position in relation to the company as a whole, let us turn to the internal organization of the research department. We find that it is common practice to build up from units, variously referred to as sections or groups each of which is composed of as many technically trained investigators and their helpers as are needed to handle a certain type of problem, provided that the number which can be effectively directed by one group leader or section

chief, is not exceeded. This maximum will ordinarily be not over six or eight technically trained men. The number of non-technical assistants will vary with the character of the work.

One of the virtues of this system hinges around and depends on these section chiefs who are key men. Their duties and qualifications merit careful examination. The section chief must, first of all, be a competent research man in his field and must be thoroughly capable of the technical supervision of the investigations conducted within his group. Second, he must be competent in handling both the internal and the outside relationships of his section. Third, he must have a sense of financial responsibility since research is a business and its cost usually is and should be budgeted. The good section chief will himself absorb the more attention consuming problems of relations with other departments and the problems of cost control and thus leave his investigators free to devote the maximum attention to research.

The degree to which a section should be specialized is open to debate. A high degree of specialization brought about by assigning to a section problems of only one kind tends to build up a personnel very capable in that field but it also promotes narrowness and inflexibility. Problems of various types are apt to occur in a differing ratio from year to year and one section is apt to find itself, in a given period, overloaded with problems in applied research and with no time for the more fundamental studies. Another may find itself in the reverse position. Long-time trends in company interest may change and the research department may find itself overstaffed with experts in a particular field who have lost the breadth and flexibility to successfully adapt themselves to new fields. This all points to the desirability of maintaining a reasonable diversity of interests in every section. By careful planning, this can

usually be done in spite of the need for assigning to a single section all problems involving expensive equipment of a special sort or involving elaborate techniques requiring long and expensive training of personnel.

The advent of intricate tools of research, which require specialists not only for their use but also for their further improvement and development, has created a problem in internal organization. A number of examples might be chosen: the spectroscope for analytical work both qualitative and quantitative, X-ray and electron diffraction equipment for structural analysis, the infrared spectrometer for the analysis of organic molecular structure, and the electron microscope. Any one of these can be set up and used in a routine way by a high-grade technician, but to realize its full value and to fully exploit its possibilities in solving new problems requires research investigators of high caliber.

If a research organization is large enough to make possible the possession of such tools, it usually proves desirable to have them in charge of a research section or group comprised not only of technicians competent to operate them but of highly trained research investigators capable of adapting old and discovering new techniques for their application. For example, if a laboratory has need for spectrographs, X-ray and electron diffraction equipment and the electron microscope, these may be well grouped in a single section staffed as recommended above. This section will provide other sections with the necessary service and collaboration on problems requiring the application of these tools. In such cases we must admit the necessity, of highly specialized sections. Fortunately, however, the danger that the individual investigators will get into a rut is not great. Their work will bring them into close contact with a wide variety of problems to which they can make contributions well beyond the scope of their speciality. Good

men on such jobs are in fact apt to attain unusual breadth.

Other types of service, some of them non-technical in character, can in many cases be advantageously centralized. Whether such centralization is profitable in a specific case will depend on individual conditions. For example, centralized shop facilities are normally essential but the extent to which the individual investigators should be allowed access to the central shop facilities or provided with separate facilities within their own sections must be decided on the basis of factors peculiar to each organization. The same is true of analytical and photographic service.

On the other hand, it is almost universal practice to have a common library staffed by trained librarians competent to conduct or assist in literature searches and abstracts, and experienced in locating and securing references not locally available. The indexing, abstracting, and circulating of periodicals is an important function of the library.

Similarly, a separate accounting department is commonly maintained. Monthly cost sheets showing expenditures by problems subdivided into payroll and other major types of expense provide the necessary data for adequate cost control and for estimating the cost of new projects.

Even the best organized laboratory will not be wholly self-sufficient and we may well consider for a moment the outside sources on which it may draw for aid.

Every industrial laboratory will find itself confronted with an occasional problem outside its established fields of investigation. The probable extent of the interest in the new line of work may not justify investment in equipment and the expense of training personnel and perhaps adding temporary personnel. In such cases it is often possible to find one of the independent research laboratories which is prepared to undertake the problem promptly and effectively. It seems likely that such

arrangements will be more and more commonly used by the industrial laboratories.

Consultants from the university faculties serve a valuable purpose in connection with industrial research. They bring a fresh viewpoint and are unworried by the pressure of industrial problems which, even under the most favorable circumstances, makes it difficult at times to maintain a good research perspective.

These contacts and the amazing freedom of contact between the industrial laboratories themselves without doubt constitute one of the potent factors in the achievements of industrial research in our country.

Having described in some detail the units and facilities from which a research organization is assembled, let us consider the pattern by which we integrate these units into a coherent whole.

The various lines of work which have been placed in the hands of the several sections can usually be grouped into two or more divisions with the sections in each division having enough in common to permit their general supervision by a division head. In a laboratory of moderate size, the division heads may be assistant directors of research while in very large organizations some further grouping of divisions may be necessary. On the other hand, where there are fewer sections, the section chiefs may report directly to the department head.

We have pursued the details of organization methods this far to show how a simple clear-cut organization, patterned along sound lines, can be set up for the technical direction of the business of research.

PERSONNEL

Selecting a pattern of organization is only a first and relatively simple step. Its effective functioning, of course, depends on intelligent handling of human relations. Research laboratories of even moderate size involve a large enough personnel to require systematic management rather

than day by day dealing with isolated problems. Success here requires that the principles of good management be firmly adhered to. A review of these principles might seem unnecessary were it not that their importance in research administration seems at times to be underemphasized. Individuals are the ultimate assets of the research organization but as individuals we have an inborn antipathy to the restraints of organization. These restraints should therefore be the minimum necessary to enable many individuals to work together effectively and harmoniously.

It follows that the first principle is to create as well as we can an environment in which each individual can and will do his most creative work. This is where the section chief makes his greatest contribution. We hire a new investigator fresh from school and turn him over to the section chief whose job it is to develop whatever qualities of initiative and resourcefulness he may possess and which are necessary to make him a valuable and productive research man. The new man will, as he develops, be entrusted with work involving substantial expenditures apart from his own salary. We therefore have two conflicting interests which the section chief must reconcile. He must determine how close a rein to hold to prevent undue loss of time and money through the younger man's inexperience without, on the other hand, destroying his initiative. Even the graduate student comes to the industrial laboratory with only his preflight and primary flying training. The section chief or his oldest investigators are the instructors who risk life, limb, and reputation making combat fliers out of the new men.

Obviously, the desired environment cannot be created unless the members of the organization know from experience that financial reward, credit for achievement, and opportunity to build a professional reputation by publication and outside

contacts are equitably handled. Here, the section chief must be supported by a sound company policy.

In this connection, a word should be given to the questionable policy of special bonuses for particular achievements. The evils of this system seem to be generally recognized and, I believe, its use is not now common. The principle is inherent when a man is employed exclusively for research work that his best effort is due the company and the results of his work their property. It would seem to follow that his reward should be based on the continuous record of his performance rather than on the outcome of a specific assignment in which chance frequently plays a large part. To abandon this principle, courts jealousies over the assignment of problems promising quick results or commanding especial attention and an aversion to undertaking the often more important long-pull jobs. Moreover, the natural desire for individual credit will lead to secretiveness rather than the full group cooperation which produces such outstanding results but which makes it nearly impossible to fairly parcel out, among the group, credit for a particular job.

This first principle—that a proper environment must be created—obviously cannot be achieved independently of those that follow.

The second principle is that the organization plan be simple and involve no overlapping or conflicting lines of authority.

The third principle is that the formal organization reflect accurately the duties and responsibilities of the individuals involved. This, of course, means that no duty or responsibility will be formally assigned on paper until careful and deliberate consideration convinces those responsible that they are willing to stand back of the commitment.

The fourth principle is that organization lines be rigidly adhered to in all matters

involving decisions and action as distinguished from interchange of information, to which latter benefit there must be no obstacle in a well conducted research laboratory. If it appears impossible to adhere to the organization lines, it is fairly certain that the second or third principle has been violated.

If these principles are properly implemented, it will be possible to meet the internal problems of the research organization and to create that unity, enthusiasm and morale which is prerequisite to effective creative research and to sound relations with other departments of the company.

THE DEVELOPMENT STAGE

I am sure that most of you have recognized a deliberate oversimplification of the problem in order to first sketch the essential elements of organization structure. This oversimplification consisted in deferring consideration of the problems which arise when research carries a new process into the commercialization stage or carries a new product or the new application of an old product into the sales field. We must now return to these problems and examine how the research organization can be adapted to their handling.

First, let us consider the commercial development of a new process through its several stages. A chemical process lends itself well as an illustration. The process has originated in a successful beaker-scale research investigation. The crock-scale test which normally follows will usually disclose difficulties requiring further beaker-scale work for their solution. Success on the crock scale will lead to a small pilot operation. New difficulties of a chemical nature due to changed rates of mixing, heating or cooling may ensue and require new work on a smaller scale. Engineering difficulties, however, will begin to assume a more prominent place and gradually these problems will become predominant. Success on the pilot scale will

be followed by a commercial-sized pilot plant and here questions of engineering, maintenance and labor assume a primary position—if we are fortunate. Sometimes we aren't fortunate and a difficulty inherent in the chemistry of the process crops out to send us back again to the beaker.

In metallurgical operations, it is not always possible to proceed by such gradual steps, witness a case where the heart of the process lay in rates of heat transfer which could be tested only on a full commercial scale. In such cases, research must be conducted on a plant scale from the outset.

Both cases illustrate the same point, that research, in the purest sense of the word, is involved until the process is working smoothly in the plant. It is involved in a diminishing degree as the work goes forward while engineering and operating are involved to an increasing extent. The transition tends to be gradual rather than abrupt and the organization problem is to make the transition from the inception of the idea by research to its routine operation by the plant as smooth as possible.

We find normally that the group who effectively carry out the laboratory-scale experiments are less proficient or even wholly inept in pilot-plant operation and are inexperienced in the problems of engineering, maintenance, and labor involved in the commercial operation.

Another group or section made up of men experienced in larger scale operations and conversely less at home with highly theoretical chemistry or physics or metallurgy and delicate laboratory-scale tests, must therefore be brought into the picture when the transition to the pilot-plant stage is made. This can be brought about very smoothly if a close relationship exists between the two sections. Such intimacy should result in a considerable familiarity with the new process on the part of what we may for convenience term the pilot-plant section, some time before the responsibility for undertaking pilot-plant

work is given to them. On the other hand, the contact of the laboratory section with the work will not terminate abruptly but their aid will be sought whenever necessary throughout the further development of the process.

In the almost Utopian situation which I have described the pilot-plant man will, when the pilot plant develops unforeseen troubles, repress his first reaction, born of the disappointment of the moment, to cuss out the laboratory theorist. The laboratory theorist on his part will refrain from jumping to the conclusion that the practical man has compromised some essential principle to escape an operating difficulty. Instead they will together impartially examine the facts and if the basic knowledge is at fault, laboratory work will be resumed. If the application of the knowledge has been imperfect, a way to improve the large-scale setup will be sought. If it appears impossible or impractical to achieve the required conditions in practice, the laboratory must seek an alternative method which can be achieved under large-scale conditions. When a relationship based on the mutual confidence of a laboratory and a large-scale investigator is built up approaching this ideal, it is an asset to be most zealously conserved and the wise research management will utilize such a team together in future problems whenever possible.

It is not, however, universally true that the same man or group cannot carry a new idea through from its inception to its commercialization. Research men vary as much in their abilities, idiosyncrasies and limitations as any other group and we naturally find that they vary in their ability to experiment on a small scale in the laboratory and in their capacity to develop an idea through successive stages into a going commercial operation.

By extended trial and observation, we can estimate the degree of each man's ability in these several phases of research

and at first glance it would seem simple to say that we will finally assign each man to the phase of the work for which he is best fitted. But when we come to grips with the realities of working with individual research men we encounter a psychological factor which we cannot afford to ignore. This is the desire which most research men have to see a new idea through to its conclusion.

This desire is a potential asset, for a man must not only have ability to do a job but he must have an interest in doing it. Keen interest and fair ability are a better combination to bet on than excellent ability and lukewarm interest and the keenest interest will lie with the man who originates an idea. If the idea must at some stage in its development be turned over to another investigator, we must, by careful handling of the transfer, engender in the man who picks up the work at its new stage a lively interest and belief in the idea. At the best, there will be a definite loss to be offset by the superior ability of the new man to handle the larger scale work.

It follows that in those cases where one man combines the abilities necessary to initiate an idea and carry it through its successive stages, nothing will be gained and much may be lost if we do not leave the job with him from start to finish.

The converse and equally important side of the same general picture is that many of the ideas warranting research projects will come from the groups assigned to pilot-scale work. The investigation of these projects will in many, if not in most cases, involve laboratory work for which the originating section is not equipped nor staffed. Here we will meet the same natural reluctance to turn the fate of the brain-child over to a foster parent—in this case as it draws its first breath. Again, the solution must lie in the existence of that indispensable mutual confidence between sections. The laboratory research group

who are asked to rear the child must remember that some future Faradays and Edisons probably looked pretty unpromising to any one but their parents at birth, and must give these foster children the same care as they lavish on their own equally scrawny looking offspring. On the other hand, the group seeking a home for their brain-child must be Spartans in those cases where closer examination reveals that the child is hopelessly malformed.

The research management is fortunate which has achieved sufficient flexibility of procedure to solve one case by having the originator of an idea carry through from start to finish and another case by making a necessary transfer of the work either at its very inception or at a later stage, without in either case losing sight of the elemental requirement that the man who conceives the idea must feel confident that it has been given a fair chance of success. Nothing can more quickly destroy the enthusiasm which is the driving force of creative research than lack of such confidence.

RESEARCH AND SALES

If we turn now from research on new processes to research leading to the introduction of a new product or the exploitation of a new use for an old product involving relations with the sales department and customers, we find the same basic factors at work in a somewhat modified form. An example illustrating this point is a case with which I happened to be closely associated. Twenty odd years ago, a customer complained that while our 99.95 per cent purity zinc was noticeably superior to the much less pure Prime Western grade he had been using in making zinc alloy die castings, the results were still far short of satisfactory. A research physical metallurgist spent some time in the customer's plant acquainting himself with the metallurgical problems of the

comparatively young and very small die-casting industry. The problem which he brought back was the basis for many years of research. The purely laboratory alloy research came first.

As time went on it became evident that the metallurgy was vitally related to the mechanics of casting because of the importance of cooling rates. A new section took over the mechanics. The new alloys which were developed had to be sold to the trade, after being first sold to the sales department. Typically, the first step was to secure the attention and interest of the metallurgists and designing engineers of actual and potential users of die castings. This required the direct effort first of research men engaged in the metallurgical development and later of those engaged in the mechanics of the process. From the outset a technical service engineer from the sales department took part in these contacts and as the job grew in magnitude others were added and they took over those customer contacts not necessitating new research. When new research was indicated a research man was brought into direct contact with the problem but, in time, first the metallurgical group and later the mechanics group were released to a greater and greater extent to devote their time to new research problems.

Those of you who have been involved in such developments will realize that this outwardly simple story actually involves many problems of interdepartmental relationships and that the efficient transfer of responsibility from research to sales requires a long period of cooperation and depends on mutual respect and confidence. It is essential to the satisfactory handling of such problems that the technical background and ability of the members of the sales department assigned to such work be of high order. That this is generally recognized is obvious from the increasing tendency to use engineers extensively in industrial sales work.

It is evident that the development which I have just described ultimately involved what is often called customer service or trouble shooting. I stated at the beginning of this talk that under certain conditions this is a function that may be effectively handled as an adjunct of research. This is apt to be true when the size of the company or of a particular branch of its business is not sufficient to warrant the duplication in separate departments of facilities and expert personnel required for the work involved. There is a further and perhaps more serious objection to separating technical sales service from research. Cases constantly recur in which recent research results which have not had time to be disseminated and assimilated by a sales service group are applicable to a customer problem and there are the corollary cases where first-hand contact with a practical problem is a valuable stimulus to research. This stimulus is so strong that almost invariably when a service group is set up outside the research department, its members are soon found to be doing research with the attendant difficulties which seem inevitable when two departments attempt to cover the same field.

On the other hand, the disadvantage of using research men for service work is serious. If there are many such demands upon one investigator his research work is seriously curtailed, not only by the actual time devoted to service work, but by the tendency to start new investigations aimed at the quick solution of customer problems. When service work is done by the research department, several means of minimizing these difficulties are employed. Sometimes the section chief, who usually does not personally carry out any experimental work, can, if he has a strong staff, spare sufficient time to handle such work. In other cases, a man fitted for the work in question may be assigned to service problems but left in his research section. By continuing some investigational work and

through daily contact with those carrying forward research in his field he keeps abreast of the latest developments and thereby maintains the unique value which a research man has in service work. Similarly, if the demands become very heavy a separate unit or section may be set up within the research department to do a limited amount of research and a large amount of service work.

Here again is emphasized the advantage of sufficient flexibility of operation to permit the handling of different cases by different methods without breaking the vital thread of organization.

TYPES OF RESEARCH ORGANIZATION

In my first reference to the grouping of sections under division supervisors, I deliberately postponed any detailed discussion of the basis for such grouping. Now having considered some of the relations between sections we can more easily assess the merits of the two general systems of grouping. These might for convenience be termed the horizontal and vertical plans. See Fig. 1. In the horizontal plan, the research department is divided into one division carrying out fundamental research and a second carrying out pilot-plant or commercial-scale work on new processes. This second group is frequently referred to as the development group. A third division is sometimes added to handle problems originating with customers and brought in by the sales personnel.

In the vertical type, the necessary subdivision is made according to the field of investigation rather than according to the scale on which it is being done as in the former (horizontal) type of organization. For example, a metallurgical company might have one group devoted to pyrometallurgical research and another to electrolytic process research. Each group would have a balanced staff capable of fundamental research in the laboratory and of pilot-scale development. Another

group dealing with physical metallurgy would be staffed for both pure research in that field and the application of physical metallurgy to casting, rolling, drawing or

away from the laboratory man as soon as it is ready for pilot-plant development, the original investigator is automatically returned to pure research. The corollary dis-

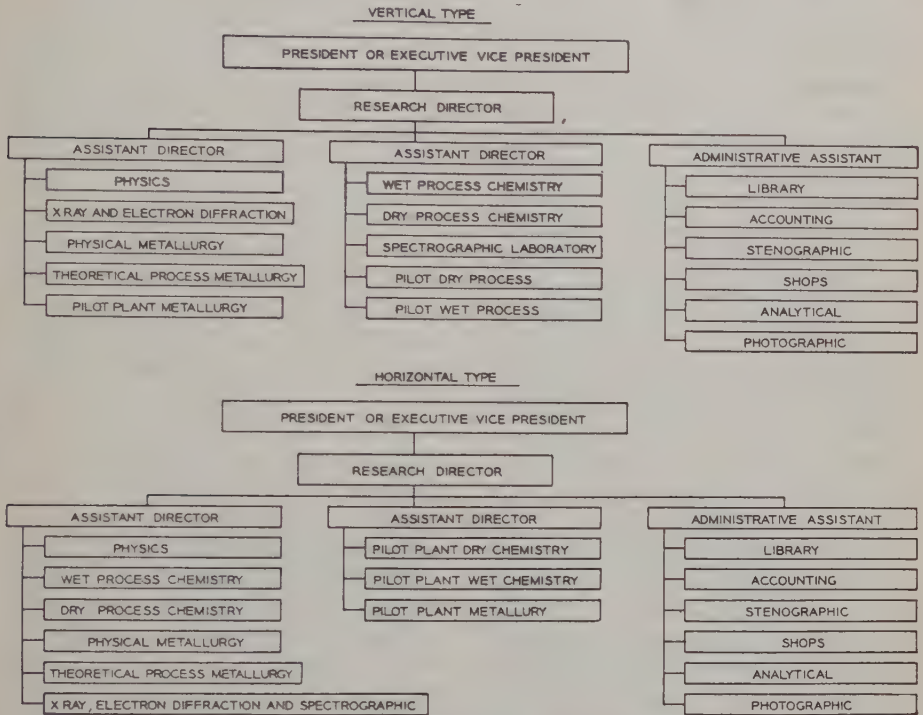


FIG. 1.—TYPICAL RESEARCH ORGANIZATIONS.

other fabricating processes either in the company's operations or in the customer's utilization of the company's products. It is evident that such a group would combine pure research and development or applied research and can easily be drawn into straight trouble shooting for either the operating or the sales departments. (See Fig. 1.)

Since both types of organization are in operation in different companies and since more than one company has tried both, it is evident that each must possess advantages and disadvantages.

The advantage of the horizontal type of division which is most often emphasized, is that by transferring a new development

advantage is that the transition from laboratory to pilot plant under this system is marked by a transfer in responsibility from the head of the fundamental research to the head of the development group. As a result the transition is apt to be more abrupt and the loss in effectiveness in carrying forward the job and the repercussion on the man who started the job are both much greater. Under this system cases are almost sure to occur where the man who carries out the research is so indisputably the best man to continue the larger scale development that it is essential to have him do so. This immediately poses a new problem. Either the man must be transferred from research to development

or the development must be carried out under research supervision. The effectiveness of the man may be closely associated with the team work which has built up between him and his supervisor on the one hand and his associates and subordinates on the other. In such a case the tendency will be to have the development handled by research and in effect shift to the vertical type of organization. If the other course is followed and the man transferred to development the difficulty of bringing him back to laboratory research is increased and the primary objective of keeping research men at research has been lost.

The advantage of the horizontal type of organization in which a separate division is set up to handle customer problems is that a buffer is set up to prevent requests for trouble shooting from diverting research men from research. The offsetting advantages of the vertical type of setup have been pointed out.

The merit of the vertical system to my mind arises from the underlying and inherent continuity between all phases of research, the fundamental, the development, and the solution of customer problems. The vertical system reflects this continuity.

These advantages and disadvantages of the two systems must be given different weights under different conditions and the ultimate choice, as I have previously said, will not always be the same.

PROGRAM PLANNING AND BUDGETING

We have now considered the original basis for the establishment of a research department, the internal structure of the research organization and some of the ways in which that structure is keyed into the external relations of the research department. There remains to consider the functioning of an organization which has been set up along the general lines described. This can be most conveniently approached by assuming that we are

looking at a research organization that is already well established and in full swing.

It is conventional at regular intervals, often annually, to review the research program and plan for the ensuing period. Let us assume that we are at the time set for such a review. Each section or group head will have prepared a report of the work completed or abandoned during the period and the status of the work still in progress. Recommendations for continuation of existing programs of work and for new work will be incorporated in the report. The heads of the research department will have digested these section reports and considered the recommendations. Thereupon, a report for the executive officers will have been prepared by the heads of the research. It is well for this report to recall briefly the reasons for having initiated each broad program of work discussed and to reassess its potential value in the light of what has been found and of possible changes in external factors.

With this statement of the current status as a starting point, the future program can be projected. No live company will lack ideas for new work. These will stem from other departments as well as research and the problem will invariably be one of selecting from an overabundance of problems those which should constitute the immediate program. The research management will prepare its recommendations as to continuation, expansion or contraction of work on existing projects and on the initiation of such new work as can be effectively handled by the available personnel.

This program will then be reviewed by the executive officers of the company. Considerations of broad company interests which they bring forward will guide possible revisions in the proposed program and the substitution of work which had been set aside for future consideration for certain problems constituting part of the originally proposed program.

The extent to which the executive officers will go into detail in the consideration of the research program will vary with the character of the work. The more directly a program aims at a specific objective such as a change in an existing process or product, the more need there will be for its consideration by the general management in the light of factors of the general company position in respect to raw materials, markets, probable capital requirements, etc. On the other hand, except for setting up some boundaries to the company's sphere of interests, the executive officers must rely on the research management and the latter must assume the responsibility for programs of fundamental research into new fields.

The financial planning or budgeting then becomes relatively simple since a fairly constant ratio between technical payroll and total expense will be found to exist for any general type of work and, except for estimating the cost of pilot-plant installations which are highly variable and are usually considered apart from the general budget, the cost of a fair sized research operation can be very accurately predicted. Certain programs will overrun and others underrun, but if the department is large enough, these will average out.

You will note my assumption that in this going organization we are contemplating neither expansion nor contraction of personnel and therefore no major change in total budget. This will not always be true and we should therefore consider the control of the total research expenditure a little further.

The primary research asset of the company is a trained and organized staff. This asset cannot be very rapidly expanded with efficiency nor temporarily curtailed without permanent loss. The prudent management of the investment in a well selected, trained, and organized research staff will therefore dictate that its expan-

sion or contraction be on the basis of long term trends and not on short term swings. It is inevitable that the research department share the effects of depressions or other major vicissitudes. If, however, during prosperous times a permissible temporary expansion of the research budget has been used to improve physical equipment and to accelerate the more expensive pilot and semicommercial-scale work, then during periods of stringency the necessary curtailment can be made with the minimum effect on the staff of investigators whose loss would mean the loss of expensive and valuable training and experience. The ratio of other expenses to technical payroll which is necessary for most efficient employment of the investigators will be reduced but this is a temporary loss which, if not too prolonged, will have no serious permanent effect.

The point which I hope I have made clear is that the decision as to the size of the total research budget should be based on long term trends and should precede consideration of the specific work to be pursued.

In discussing at such length the review of the program at the beginning of the budget period, there is, of course, no intent to imply that the research program is given consideration only then. The purpose is rather to emphasize that in spite of the continuous reviewing and adjusting of individual parts of the research program through the constant contact of the research management with the other departments and officers, a comprehensive periodical review of the program as a whole is beneficial. (See Fig. 2.)

Both in the week-to-week and in the less frequent periodical reviews of research programs, we must constantly guard between two dangers. The one is that the persistence which is essential to success may lead us to continue an investigation after good judgment dictates its abandonment. An analogous error is to continue unimportant

secondary investigations after the need for them or any likelihood of their proving valuable in their own right has disappeared. This is usually done on the tenuous plea

spend our money where there is some right to hope for a worth while return.

The second danger is the opposite of the first and more serious. Distant pastures look greenest in research quite as much as in any other pursuit. Most new ideas follow a rather stereotyped progression. The first stage is the vision of a new thing serving a new purpose and the first quick mental appraisal is apt to set the value in the millions. This is the stage at which promoters pick ideas and take them to market. No promoter ever peddled an idea worth less than a million and promoters don't usually get hold of ideas after they have actually been found to be worth millions. We may safely conclude therefore that they pick these frail blossoms in the early morning before the sun has struck them.

The second stage is to put the idea through some very rudimentary tests, not in the laboratory but in the library and across the conference table. One of the great merits of organization in research is this opportunity for early appraisal of new ideas by alert imaginative men of varying training and viewpoint. This accomplishes two equally important things. It frequently brings to light fatal fundamental flaws in the idea and thereby avoids the waste of attempting to develop it. This is a negative virtue but this free-for-all criticism just as frequently has the constructive effect of bringing out other supplementary or independent ideas, of suggesting additional possible applications of the idea, and of suggesting means of overcoming immediately apparent difficulties. Often the originator of the idea would arrive at these solutions slowly, if at all, because of some limitation in his training or experience.

A few ideas survive the conference and are passed on to the laboratory with great optimism. We all tend to wait with bated breath for a successful result. After all, sometimes we do hit a bonanza that can be very quickly recognized. But more often we find it better to go right on breathing;

I.—Financial Control

First Step

Determination of permissible budget total by Executive Heads of Company.

Second Step

Translation of total dollars to manpower that can be maintained with proper margin of safety for contingencies.

II.—Research Program Planning

First Step

Review of existing projects.

Second Step

Compilation of new proposals from all sources within and without Research.

Third Step

Consultation by Research Administration with executives and other departments to help form basis for (4) and (5).

Fourth Step

Selection of projects for abandonment, curtailment or early conclusion.

Fifth Step

Selection of most important new projects which can be carried out with available manpower.

III.—Frequent Review of Research Program by Research Staff

First Step

Through continuous supervision.

Second Step

Through regular reporting of all projects.

IV.—Continuous Contact Between Research and Other Departments

First Step

To transmit useful findings to other departments.

Second Step

To secure facts needed to guide useful application of findings

FIG. 2.—STEPS IN RESEARCH CONTROL.

that to drop the job leaves a loose end. A brief report will serve to tie a knot in the loose end. I am not ignoring the fact that valuable discoveries sometimes result from work along the most unpromising lines, but the number of fields in which we can work is almost infinite and we must try to

in fact, we would do well to take a deep breath and reach down for some real money with which to embark on a long development. At this point we must consider carefully whether the odds warrant starting on a thoroughgoing investigation; if so, and we have the men available, we settle down to a long hard grind, punctuated usually by many more discouragements than favorable results. Outside interest drops from fever heat to normal and time passes. And then some bright morning, another new idea is born. It passes the first tests and is ready for the laboratory, but every one is busy. Interest on the new idea is at fever heat. What can we stop work on to make room for it?

So here we are face to face with the second danger, the danger that we will drop the first idea because we have found out just what the problems are which must be solved and just how long it may take to finish the job. The stake may still appear just as large and the odds of succeeding may be good, but we are attracted by the glamour of the new idea and tempted to abandon the old. No suitable men can be freed and we are not in a position to expand our organization. Perhaps this is the commonest and most difficult dilemma in which the research management finds itself, and while the proper course to follow is evident it is nonetheless hard. First, we will make sure that we have, in fact, stopped those projects which should be stopped according to the principle suggested a few minutes ago. If we have not already done this, it may be possible in this way to secure the needed personnel. If we fail in this, we must accept the hard fact that each of the projects under way was justified in its inception and that the justification persists after some period of work. This work has probably brought to light at least part of the difficulties not originally apparent and hence the appraisal of these old projects is more reliable than the appraisal of the new idea. Finally, we

must recognize that we have made an investment in each of the old projects which will be lost, certainly in part, probably completely, if the work is stopped. Even a temporary interruption of an investigation is costly. The enthusiasm of the investigator suffers, trained non-technical personnel may be dispersed to other jobs, and the whole momentum of the work is lost. We all of us need as a wall motto a reminder that starting new projects is excitingly pleasant but that only finishing old ones pays dividends.

REPORTS

I am approaching the end of my talk without having touched on a most important point; namely, the reporting of research work. The product of research is an intangible thing, knowledge. It can be delivered by word of mouth, and is and must be, to a large extent, so transmitted. The ability to talk clearly and concisely is, therefore, a prime asset in a research man. But civilization has long ceased to rely on oral reporting and the ability to write a good report is an essential qualification of a good research investigator. I think perhaps we blame our educational system too largely for the deficiencies of our technically educated men as writers. While a certain technique of rhetoric and composition is necessary, clear thinking is the foundation of good writing. Formal education is a more reliable means of achieving the technique than the foundation.

When a good, clear thinking investigator doesn't write a good report, it is probably due to a lack of desire rather than a lack of ability, and the man must be educated to realize the vital necessity of promptly presenting well-written reports. The steps in this educational process are first to make him realize that he has failed to take his product to market if he doesn't write a report; second, that it won't sell unless it is well presented. He must be made further to realize that the men whom he wants to

have read and understand what he has done have a very slight knowledge or poor recollection of why the job was ever started and what it's all about, and their

Abstract

A concise statement of the purpose and scope of the investigation and of the conclusions reached and recommendations for action or further work.

Report Proper

Title Page

Showing names of investigators, dates between which work was carried out and numbers of original notebooks.

Introduction

A full clear statement of the origin, purpose and scope of the work.

Summary

A concise factual statement of the results.

Conclusions

A clear statement of the author's conclusions from the data.

Experimental Work

A concise description of methods and apparatus used or reference to previous description.

Sufficient data to support the conclusions, including, of course, any significant results contradictory to the conclusions.

Appendix

Further data of sufficient importance to make reference to the original notebooks inadequate.

FIG. 3.—FORM FOR REPORTS.

memory must be courteously refreshed. He must not forget that if he thoroughly understands his subject he can make the essentials of his story, no matter how technical it may be, clear to any other intelligent person, no matter how non-technical the latter may be. And above all, he must, with all due modesty, want to make the people who should be interested understand his story.

A system must be set up to insure that reports are written and they must be

reviewed to insure that the research department is willing to have them issued as its product, but the best way to make the system work will be to educate the investigators to want to write good reports.

For the convenience of the reader, a uniform arrangement should be adopted for all reports. Fig. 3 outlines a form which has worked out satisfactorily in more than one laboratory. It should hardly be necessary to say that every report should be accompanied by a short clear abstract. It may prove convenient to have only the abstracts regularly circulated to those who may be interested, with the full report available on request, through the company library.

CONCLUSION

I have discussed organization, and have tried to point out some of the factors which seem vital in the primary conception of the function of research, in the internal structure of the research department, in the control of research, and in the reporting of research. I have tried to emphasize that there is no one best and unchangeable pattern for organizing a research department. Organizations are structures built of individuals and an organization chart is only the post factum blueprint of a structure built on the job from the best material which we can secure. If the material is good and the structure soundly put together, we can leave the organization chart to take care of itself.

It is my hope that this attempt to analyze some of the stresses and strains in research structures will be of some use to those of you who may have the problem of building a research organization from your own materials to serve your own purposes.

Microradiography—a New Metallurgical Tool

By S. E. MADDIGAN,* JUNIOR MEMBER A.I.M.E. AND B. R. ZIMMERMAN†

(New York Meeting, February 1944)

Most metallurgists are well acquainted with the contributions already made to the study of metals by the use of X-rays. On the one hand, the radiographic method is constantly becoming of increasing importance as a nondestructive testing procedure, while on the other hand the techniques of X-ray diffraction have made important contributions to the fundamental knowledge in studies of phase diagrams, stress conditions, and so forth. A new, and as yet insufficiently appreciated, tool exists in the application of microradiography to alloy structures.

This new procedure in many respects bears the same relation to microscopic investigations as does macroradiography to the gross inspection of metal surfaces. However, where macroradiography is used ordinarily to determine the soundness of the metal structure, this new method can be used not only to investigate micro-unsoundness but also to examine the distribution of the constituent elements within the body of the alloy. When combined with the normal procedures of microscopy, this offers a technique of great potential power. It is intended in this paper to present a few examples of copper-base alloys demonstrating the additional knowledge obtained from the microradiographic method.

The detection of micro-unsoundness is demonstrated in Fig. 1 for a sample of cartridge brass as cast. The sample ap-

peared quite sound when viewed under the microscope, but in reality was thickly populated with minute voids. This application of the method conforms in every way to conventional large-scale radiography and has been used to facilitate production of metal for vacuum devices.¹

The true potentialities of the technique are revealed by comparison of Figs. 2*a* and 2*b*, which are respectively a photomicrograph and a microradiograph of a cast alloy of 80 per cent Cu, 10 per cent Sn, 10 per cent Pb. The remarkable difference in appearance provides some concept of the additional information this method may yield when used as an auxiliary to microscopic studies. Fig. 2*a* shows two phases of the copper-tin system plus segregated lumps of lead. Fig. 2*b*, on the other hand, shows with exceptional clarity the actual dendritic growth of the metal crystals during solidification.

The practice of microradiography depends upon the laws of absorption of X-rays. This subject has been reviewed thoroughly in recent papers,^{1,2,3} but for clarity a brief resumé will be given here. As is well known, when a beam of X-rays is transmitted through a layer of homogeneous material, the intensity is reduced according to the relation:

$$I_1 = I_0 e^{-\mu_1 t_1}$$

where I_1 is the transmitted intensity,

I_0 is the incident intensity,

μ_1 is the linear absorption coefficient of the material,

t_1 is the thickness of the material.

¹ References are at the end of the paper.

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* Research Physicist, Chase Brass and Copper Co., Waterbury, Connecticut.

† Assistant, Physics Laboratory, Chase Brass and Copper Co.

When the layer of material contains an inhomogeneity of thickness t_2 and absorption coefficient μ_2 , the transmitted beams through the homogeneous matrix and

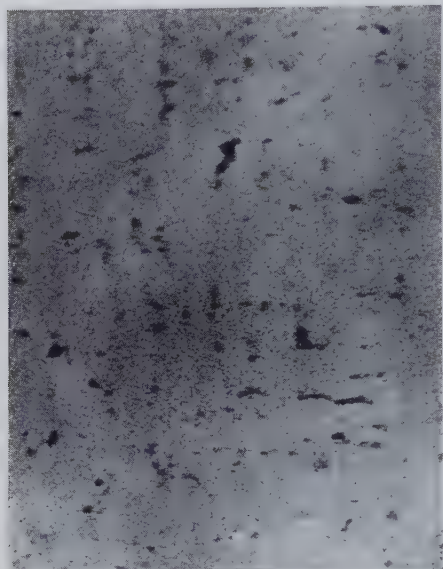


FIG. 1.—SOUND CARTRIDGE BRASS SHOWING MINUTE VOIDS.

Mo radiation, 42 kv. $\times 100$.

Original magnifications given: reduced approximately one third in reproduction.

through the region of the inhomogeneity are related by the expression:

$$I_1/I_2 = e^{-(\mu_1 - \mu_2)t_2}$$

where $(\mu_1 - \mu_2)$ is the difference in linear absorption coefficients for the matrix and the inclusion. Tables of absorption coefficients of the elements are given in most standard references on X-rays.

In most metallurgical problems it is necessary to know the absorption coefficient for a solid solution of two or more elements or for some other alloy phase. For a given phase of density d consisting of two elements of amounts by weight X and Y and mass absorption coefficients ρ_x and ρ_y , the linear absorption coefficient is calculated from the relation:

$$\mu = d \frac{(X\rho_x + Y\rho_y)}{X + Y}$$

The contrast with which such inhomogeneities becomes visible is dependent only on the value of $(\mu_1 - \mu_2)$ and of the thickness t_2 of the inhomogeneity. The mass absorption coefficient ρ varies with increasing wave length according to an approximately linear relationship on a log-log plot except at the absorption levels as shown in Fig. 3. From these curves it can be seen that the absolute difference between the absorption coefficients for two materials is, in general, greater for X-rays of longer wave length. As a result, the earlier work on microradiography was done with long wave-length X-rays, using extremely thin samples enclosed in special vacuum equipment. This was a serious deterrent to its application to most metallurgical problems.

The credit for devising a practicable and relatively simple technique belongs to Clark^{1,2} and his collaborators, who showed that the use of characteristic X-radiations of intermediate wave length could yield high sensitivity with greatly reduced exposure time. As shown in Figs. 3 and 4, at a wave length corresponding to the K absorption level for one of the elements, a sudden jump occurs in the value of the absorption differential $(\mu_2 - \mu_1)$. For the Cu-Fe absorption differential described in Fig. 4, the value of $(\mu_2 - \mu_1)$ is at first negative with steadily decreasing absolute value as the wave length is decreased. At the K absorption level for Fe (1.739 Å.) an abrupt and discontinuous change occurs and $(\mu_2 - \mu_1)$ assumes a high positive value. The quantity remains positive but decreases in magnitude until a second abrupt change occurs at the K absorption level for Cu (1.377 Å.). For all points below this wave length the value is again negative with a magnitude that steadily decreases with decreasing wave length. The absolute magnitude of the absorption differential is greater in the band from 1.377 to 1.739 Å.

than it is at even the longest usable wave lengths (Fig. 4). This allows increased sensitivity and contrast in the radiograph.

It was demonstrated by one of the present authors,³ however, that the use of such characteristic radiations must be

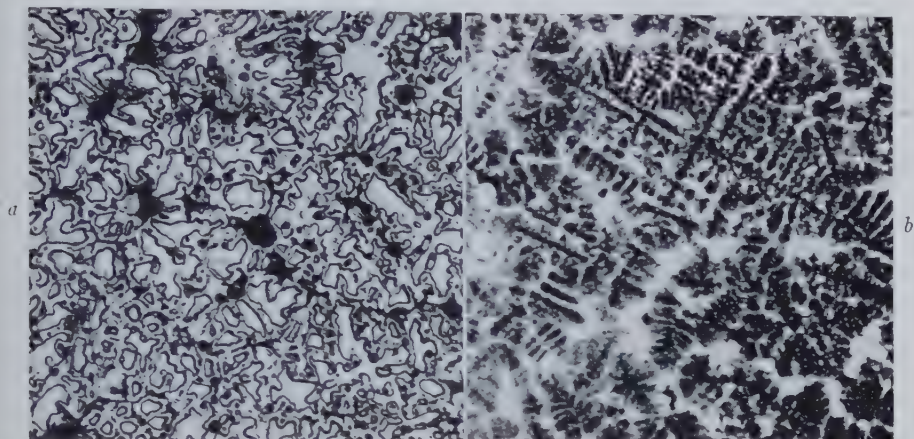


FIG. 2.—ALLOY I: 80 PER CENT COPPER, 10 PER CENT TIN, 10 PER CENT LEAD.

a. Photomicrograph. $\times 75$.

b. Radiograph: Co radiation, 30 kv. $\times 100$. Copper rich regions are dark; tin-rich regions and lead are light.

Original magnifications given, reduced approximately one third in reproduction.

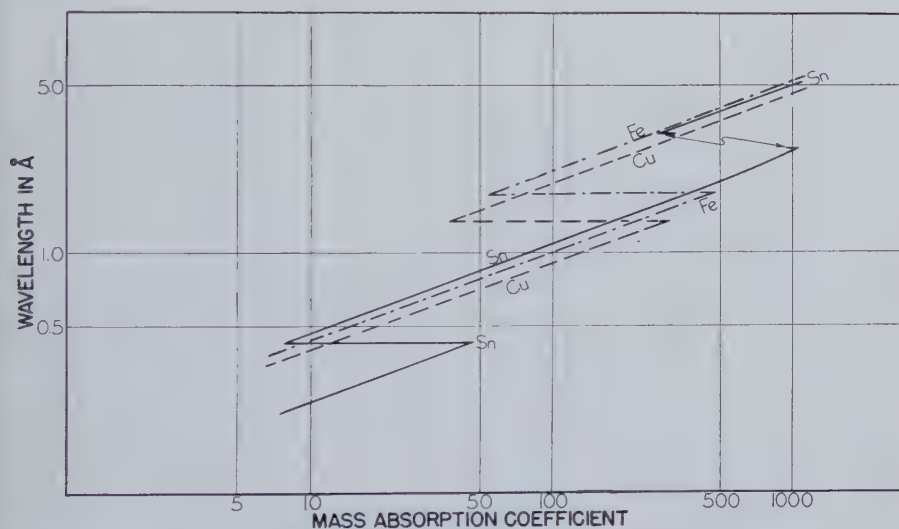


FIG. 3.—MASS ABSORPTION COEFFICIENT AS FUNCTION OF WAVE LENGTH FOR COPPER, TIN AND IRON.

As was shown by Clark and Shafer,² the segregated Cu compound in an Al-Cu alloy actually gave better contrast with Mo radiation than was obtainable from radiation of somewhat longer wave length.

accompanied by considerable discretion in regard to the voltage applied to the X-ray tube. As will be explained later, the contrast obtainable can be seriously decreased by a poor choice of operating potential.

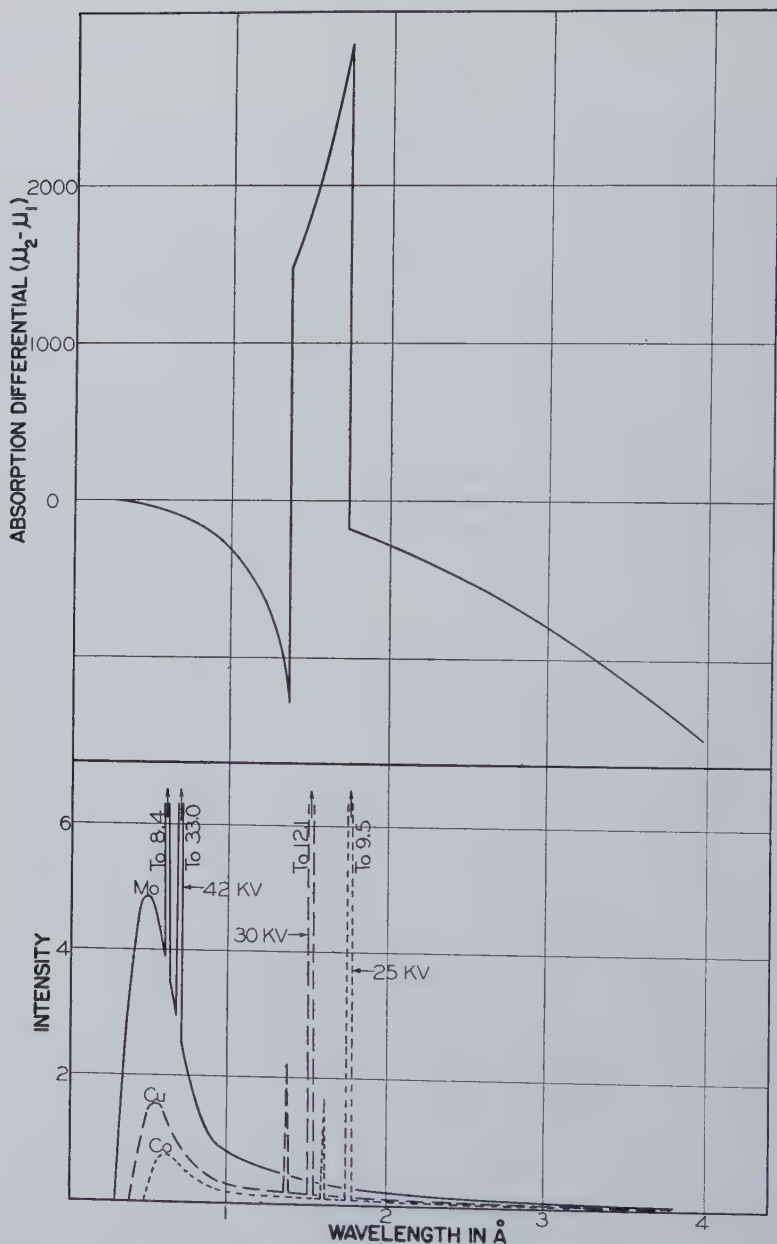


FIG. 4.—LINEAR ABSORPTION DIFFERENTIAL BETWEEN IRON AND COPPER AS FUNCTION OF WAVELENGTH CORRELATED WITH X-RAY EMISSION CURVES FOR MOLYBDENUM AT 40 KV., COPPER AT 30 KV, AND COBALT AT 25 KV.

(Note that the strong $\text{CoK}\alpha$ line falls to the right of the sensitive region, but the weak $\text{CoK}\beta$ falls within the sensitive region. This must be considered in the analysis. See discussion of Fig. 10 and Addendum concerning Figs. 15 and 22, page 58.)

In the curves for absorption differential ($\mu_2 - \mu_1$) discussed here and later, a negative value implies that the second constituent is less absorbing than the copper-rich matrix and therefore details of the second constituent should appear dark on a lighter background in the matrix. The contrast will depend on the magnitude of ($\mu_2 - \mu_1$) and on the size of the second constituent. For a given size of inclusion and negative values of ($\mu_2 - \mu_1$) the greatest contrast would be produced by a void or air pocket. For positive values of ($\mu_2 - \mu_1$) the second constituent should appear light against a darker background. For such cases the contrast can become very high.

As shown in Fig. 4, the emission from an X-ray tube consists not only of the monochromatic characteristic radiation but also of a "white" or "continuous" background containing many wave lengths. The intensity curve for this continuous radiation is analogous to the black-body curve for radiation from a hot body and both the intensity and limiting wave length depend upon the applied voltage. Superimposed on this continuous radiation is the high-intensity characteristic radiation that can be considered as essentially a single wave length. Thus, to obtain a true picture of the absorption of an X-ray beam in a material, it is necessary to consider absorption of all wave lengths in the white radiation as well as that of the characteristic wave length.

A similar consideration shows that in studying inhomogeneities it is necessary to evaluate the absorption differential ($\mu_2 - \mu_1$) not only for the characteristic radiation but also for the various wave lengths contained in the white radiation. The photographic contrast is then dependent not on (I_2/I_1) for the characteristic rays, but on $\int I_2/\int I_1$ where the integration is made over all wave lengths contained in the X-ray beam.³

The intensity of emission from an X-ray tube, including that of the characteristic

rays, increases with increasing voltage and at the same time the limiting wave length of the background shifts to lower values. A correlation of the variation of absorption with wave length (Fig. 3) with the emission curves (Fig. 4) shows that the higher the voltage, the more penetrating, and therefore the more important, becomes the radiation in the vicinity of the background peak. Suppose that in the incident beam the background peak has appreciable intensity and the absorption differential in the material is low as compared with the respective values for the characteristic radiation. As a result, the transmitted intensity of the background peak becomes comparable to that of the characteristic radiation and the photographic contrast obtainable from the characteristic rays alone is greatly reduced by the presence of the background peak. Thus, it is evident that the voltage as well as the target element must be considered in obtaining maximum contrast without excessive exposure time.

Emission curves at suitable voltages are shown in Fig. 4 for Mo, Cu and Co targets. Comparison with the absorption differential curves for Cu-Fe alloys shows that high contrast is produced by Cu radiation at the appropriate voltage, since most of the emitted intensity falls in a region of high values for ($\mu_2 - \mu_1$). For the Mo and Co targets, on the other hand, the characteristic radiation is in a region of low negative absorption differential and by itself would produce negligible contrast. At an unsuitable voltage, however, some of the background peak might lie in a region of appreciable absorption differential and result in a slight but visible contrast.

EXPERIMENTAL PROCEDURE

The general experimental procedure used has been outlined previously in some detail by Clark^{1,2} and by one of the present authors.³ For coherence, however, a brief outline will be given here. Three X-ray

tubes were available in this laboratory with Co, Cu and Mo targets. These were operated on self-rectified voltage. The linear absorption coefficients for the three

amination and scribing of a suitable region, they were mounted in lucite moldings with the unprepared surface facing outward; then in a lathe this second surface was

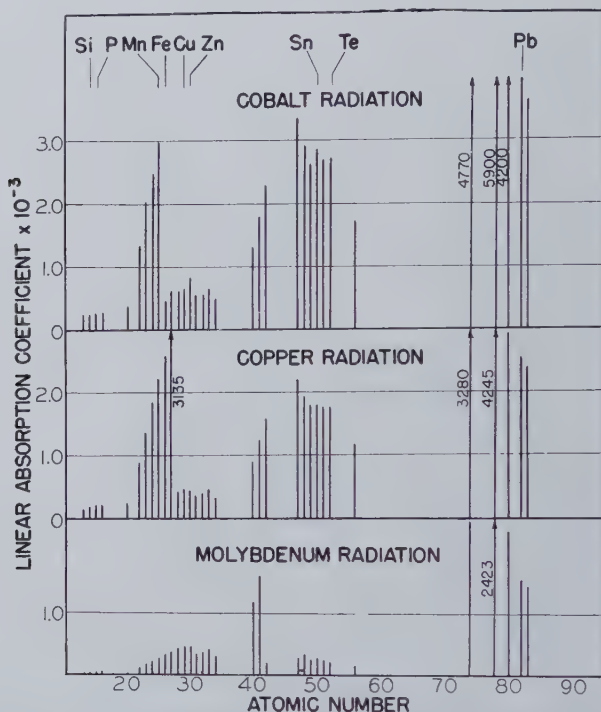


FIG. 5.—LINEAR ABSORPTION COEFFICIENTS OF CHARACTERISTIC RADIATIONS OF COBALT, COPPER AND MOLYBDENUM IN VARIOUS ELEMENTS.

characteristic radiations in a large number of elements are shown in Fig. 5. From the values in this figure, absorption differentials between any two elements can be evaluated, and in this way it can be determined which X-ray tube will give the greatest contrast for the alloy under investigation. The choice of voltage is dictated by an examination of the absorption differential curves and of the X-ray emission curves in Fig. 4.

Specimens were prepared by a procedure available in most metallographic laboratories and previously described in some detail. Briefly, flat samples of essentially uniform gauge were polished on one surface for metallographic examination. After ex-

turned down parallel to the polished face until the sample reached a gauge of about 0.010 in. From this thickness it was hand polished on emery paper of varying grades until approximately the desired gauge was reached (0.005 in. or less) or until the specimen began to loosen in the lucite mounting. If the latter occurred, the specimen was removed from the molding, remounted on a rubber stopper⁴ with Cenco label varnish and the reduction in gauge continued as before. The surface was finally finished off on French papers to the $\frac{3}{6}$ grade, using an oil film for the final stages. The entire procedure required about the same time of preparation as for a good metallographic specimen.

The foil-like specimen, after removal from its mounting, was placed behind a $\frac{1}{8}$ -in. hole in a brass plate, in which position the selected region was radiographed.

rated from the metal specimen only by an intervening single layer of black paper. Details of development have been given elsewhere. The radiographs were enlarged

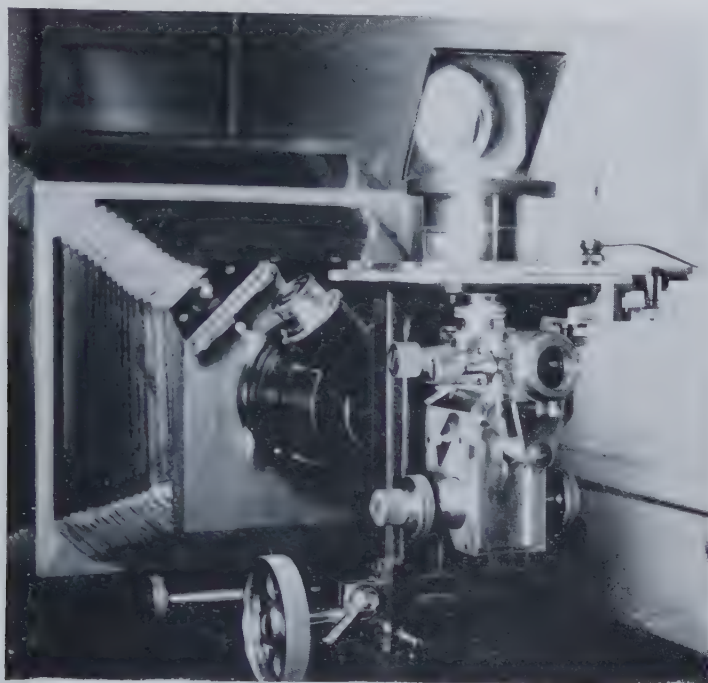


FIG. 6.—MICROSCOPE ARRANGED FOR ENLARGING RADIOGRAPHS.

Eastman type 548-o spectrographic plates (high resolution, 500 lines per mm.) were used throughout, with the emulsion sepa-

by the use of a metallographic microscope with transmitted light by placing the radiographic plate on the stage of the microscope and using a 45° mirror to direct the rays from the light source through the emulsion of the radiograph.

TABLE 1.—*Approximate Compositions of Alloys*

Alloy No.	Cu	Zn	Sn	Pb	Fe	Miscellaneous
I	80		10	10		
II	62	35	3			
III	66.5	27.9	3.9	1.7		
IV	61.7	37.7			0.59	Mn 0.003
V	59	38	0.95		1.9	Si 0.035
VI	64.2	33.4	0.4		0.9	Mn 0.1, Al 1.
VII	60.6	37.8	0.8		0.8	Mn 0.01
VIII	67.3	18.8			2.5	Mn 4.7, Al 6.7
IX	62	34.8		3.2		
X	95.6	1		0.4		Si 3
XI	90.5					Te 0.5
XII	88.5	9.7				Te 0.5, Ni 1.1, P 0.22
XIII	88.5	9.7				Te 0.5, Ni 1.1, P 0.22
XIV	70	30			?	
XV	90	10			?	Mn ?

Fig. 6 shows the assembly for this procedure, in which the microscope objective and the small exposed circles on the radiograph can be seen faintly reflected in the 45° mirror. A magnification of 100 diameters was found most suitable for the greater part of the work, although higher magnifications may be used, up to about 300 diameters.

A large number of copper alloys have been investigated by this procedure. Some of the more interesting and illustrative

results are shown and discussed in the following pages, in order to indicate the scope of the technique. Some of the examples studied were taken from defective material

Approximate compositions are given in Table 1 for the various alloys investigated. Table 2 presents values for phase composition, density and absorption differential

TABLE 2.—*Approximate Compositions and Absorption Differentials for Phases Discussed in the Text^a*

Alloy	Fig. No.	Radiation	Major Phase			Minor Phase			$\mu_2 - \mu_1$
			Composition	Sp. Gr.	μ_1	Composition	Sp. Gr.	μ_2	
1	2b	Co	97 Cu, 3 Sn	8.9	785	76 Cu, 24 Sn	9	1,372	587
2	8b	Co	63.2 Cu, 35.5 Zn, 1.3 Sn	8.5	725	61.5, 34.5 Zn, 4 Sn	8.5	801	76
	8c	Mo			439			439	0
3	9b	Cu	70.7 Cu, 29 Zn, 0.3 Sn	8.5	474	65 Cu, 29 Zn, 6 Sn	8.5	576	103
	9c	Mo			442			433	9
4	10b	Cu	62 Cu, 38 Zn	8.4	473	99.4 Fe, 0.6 Mn	7.85	2,471	1,999
	10d	Co			692	90 Fe, 10 Mn	7.85	2,451	2,068
	10c	Mo			442	99.4 Fe, 0.6 Mn	7.85	473	219
						90 Fe, 10 Mn	7.85	751	59
						99.4 Fe, 0.6 Mn	7.85	300	142
						90 Fe, 10 Mn	7.85	264	178
5	11b	Cu	60 Cu, 39 Zn, 1 Sn	8.4	490	100 Fe	7.85	2,472	1,982
	11d	Co			719	66 Fe, 34 Si	6.1	1,388	898
	11c	Mo			708	100 Fe	7.85	455	264
						66 Fe, 34 Si	6.1	415	304
						100 Fe	7.85	300	408
						66 Fe, 34 Si	6.1	167	541
6	12b	Cu	65 Cu, 33.5 Zn, 0.5 Sn, 1 Al	8.5	484	100 Fe	7.85	2,473	1,989
						90 Fe, 10 Mn	~7.8	2,234	1,750
7	13b	Cu	61 Cu, 38 Zn, 1 Sn	8.4	490	100 Fe	7.85	2,473	1,983
						99 Fe, 1 Mn	7.85	2,471	1,981
8	15b	Cu	73 Cu, 20 Zn, 7 Al	~7.7	421	65 Mn, 35 Fe	~7.5	2,326	1,805
	15c	Co			957			2,273	1,310
	15d	Mo			372			266	106
9	16b	Cu	64 Cu, 36 Zn	8.5	477	100 Pb	11.4	2,622	2,145
10	17	Cu	99 Cu, 1 Zn, 7 Si	8.9		? Pb, ? Si			
11	18b	Cu	100 Cu	8.9	481	50 Cu, 50 Te	~6 ^b	987	506
	18c	Cu				50 Cu, 50 Te	~6 ^b	987	507
12, 13	19b	Cu	90 Cu, 10 Zn	8.8	480	26 P, 74 Ni	6	319	161
	20b					50 Cu, 50 Te	~6 ^b	259	187
	19c	Mo			446	26 P, 74 Ni	6	226	221
14	21a	Cu	70 Cu, 30 Zn	8.	474	100 Fe	7.85	2,472	1,998
	21b	Co			694			455	239
15	22a	Cu	90 Cu, 10 Zn	8.8		? Fe, ? Mn			
	22b	Co							
	22c	Mo							

^a The phase compositions indicated are approximations and are complete only to the extent required by the argument. In some cases, such as alloy 1, the extremes of the freezing range were necessary and have been given; in others, such as alloy 14, only an average composition for the matrix is listed, since variations in absorption in the brass were small compared with the difference between matrix and inclusions. In alloy 8 all the Mn was assumed concentrated in the segregated particles, though this was not necessary to explain the effect. Where definite compounds were assumed others might be equally valid; e.g., Ni_2P , Ni_3P or Ni_5P_2 rather than Ni_3P_2 . The general argument would not have been changed by such alterations.

^b Estimated from ionic radii.

and should not be considered as characteristic of a commercial product.

The photomicrographs and microradiographs displayed are not always at the same magnification, but were taken in the same general region and are similarly orientated with respect to metal flow and other conditions. In some cases a scribed reference circle may be seen.

where the alloy structures were readily deduced from the literature. In other cases, the values offered are for the individual elements concerned.

DISCUSSION OF RESULTS

The alloys investigated fall into several general classifications and shall be so discussed here.

Tin in Copper Alloys

The absorption differential curves are shown in Fig. 7 for Cu vs. Sn as well as for the actual limiting compositions of the several alloys. These curves have the same general shape but differ somewhat in height; thus the conditions for maximum contrast are identical, but the contrast obtained will diminish with decreasing Sn content. The radiation from either Cu at 30 kv. or Co at 25 kv. gives excellent contrast, whereas the contrast with a Mo target at 42 kv. will be very small.

In alloy I (80 Cu, 10 Sn, 10 Pb, as cast) already mentioned, solidification occurred in a composition range from 97 per cent Cu, 3 per cent Sn to 76 per cent Cu, 24 per cent Sn with the Pb thrown out as segregated clumps. The absorption differential for the limiting compositions of the Cu-Sn alloy was 590 for Co K-radiation. During solidification the crystals begin to grow with spines of the copper-rich limiting composition while the final interdendritic material (neglecting Pb) contained the tin-rich limit of the composition range. The high value for the absorption differential brings out in Fig. 2*b* with excellent contrast the dendritic growth of the cast structure. At room temperature no large redistribution of Sn had occurred, but the alloy consisted of two phases with a considerable composition range for each. This resulted in a smearing of the detail for optical investigations so that the dendrites are not clearly indicated in Fig. 2*a*.

Alloy 2 was a forged structure in an alloy of Cu-Zn-Sn. During solidification only a small variation in Cu and Zn occurred⁵ while the Sn content varied in the range 1.3 to 4 per cent. At room temperature the forged structure shown in Fig. 8*a* consisted of elongated grains of the alpha phase with an intergranular eutectoid of alpha and gamma phases. For the limiting compositions of this structure the absorption differential was 76 with Co K-radiation. The

microradiograph in Fig. 8*b* shows the tin-rich regions as light against the darker copper-rich material. The appearance of the radiograph can be readily rationalized with that seen in the photomicrograph. The detail is almost obscured in Fig. 8*c* (Mo-K radiation). The value of $(\mu_2 - \mu_1)$ for Mo K-rays was zero, which would not provide any contrast. The slight detail observable was due entirely to background radiation.

The material of specimen 3 consisted of Cu-Zn-Sn-Pb which solidified in the approximate composition range⁵ 71 Cu, 29 Zn, 0.3 Sn to 65 Cu, 29 Zn, 6 Sn with practically no change in the Zn content (Pb a separate constituent). Fig. 9*a* shows the alloy in a forged condition with grains of the alpha phase, intergranular islands of alpha-gamma eutectoid, and dark clumps which presumably are Pb. The absorption differentials are given in Table 2. The microradiographs of Figs. 9*b* and *c* can be rationalized to agree with Fig. 9*a*, but give some additional information. The Pb is revealed as small white particles (Fig. 9*c*) but in addition there are many dark particles of the same average size, which indicate minute voids. Thus many of the dark spots identified in Fig. 9*a* as Pb may have been voids. The tin-rich phase is light against the darker copper-rich phase in Fig. 9*b*; this was much more continuous in nature than was indicated in Fig. 9*a*.

Iron in Copper Alloys

Studies of Cu alloys containing Fe offer a particularly strong illustration of the power of the microradiographic method. The absorption differential curve of Fig. 4 shows a highly sensitive band containing the wave length of Cu K-radiation but not that of Co K α or Mo K. Thus strong contrast should result for Fe segregations inspected with Cu K-radiation, but no detail should be visible with either Mo or Co provided the tube voltage

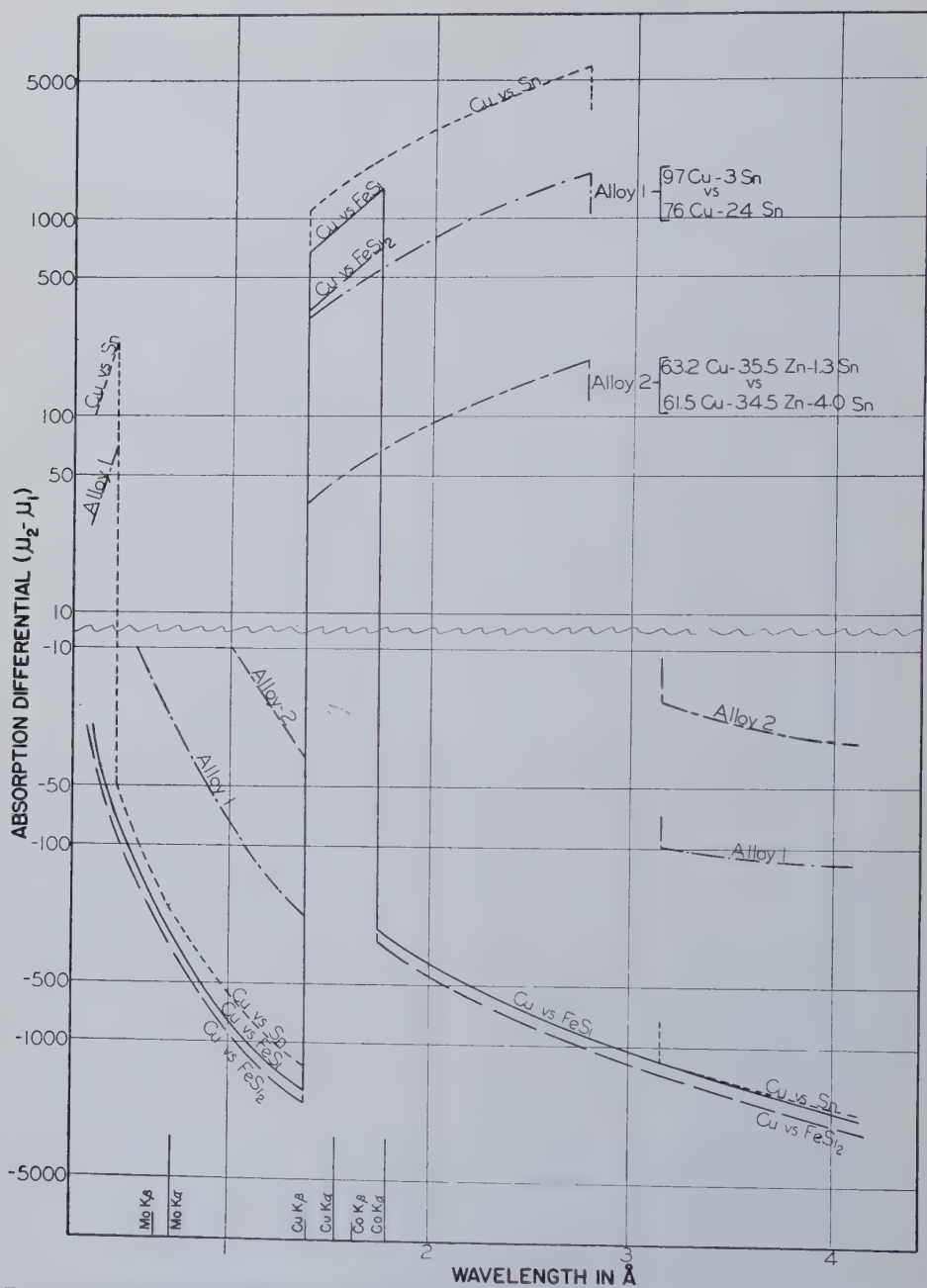


FIG. 7.—ABSORPTION DIFFERENTIALS BETWEEN COPPER AND TIN, IRON SILICIDE, AND BETWEEN THE LIMITING COMPOSITIONS OF THE FREEZING RANGES IN ALLOYS 1 AND 2.

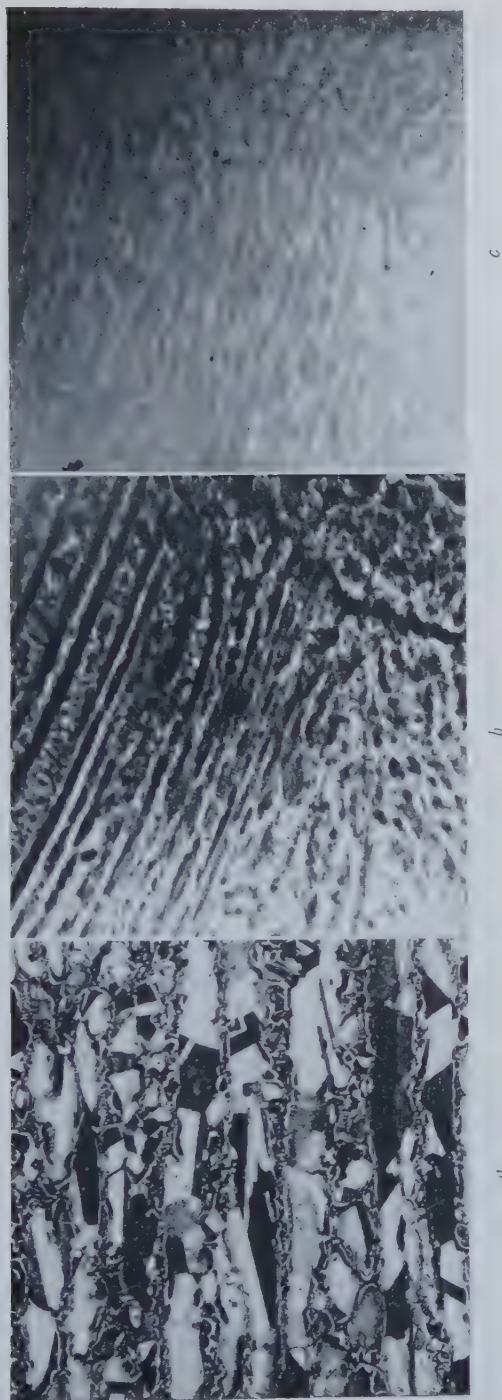


FIG. 8.—ALLOY 2 (65 PER CENT COPPER, 35 ZINC, 3 TIN).

- a.* Photomicrograph showing alpha and gamma phases. $\times 500$.
b. Radiograph: Co radiation, 30 kv, $\times 100$. Tin-rich regions light against the dark copper-rich regions.
c. Radiograph: Mo radiation, 42 kv, $\times 100$. Same details as *b* but much less contrast.
Original magnifications given; reduced approximately one third in reproduction.

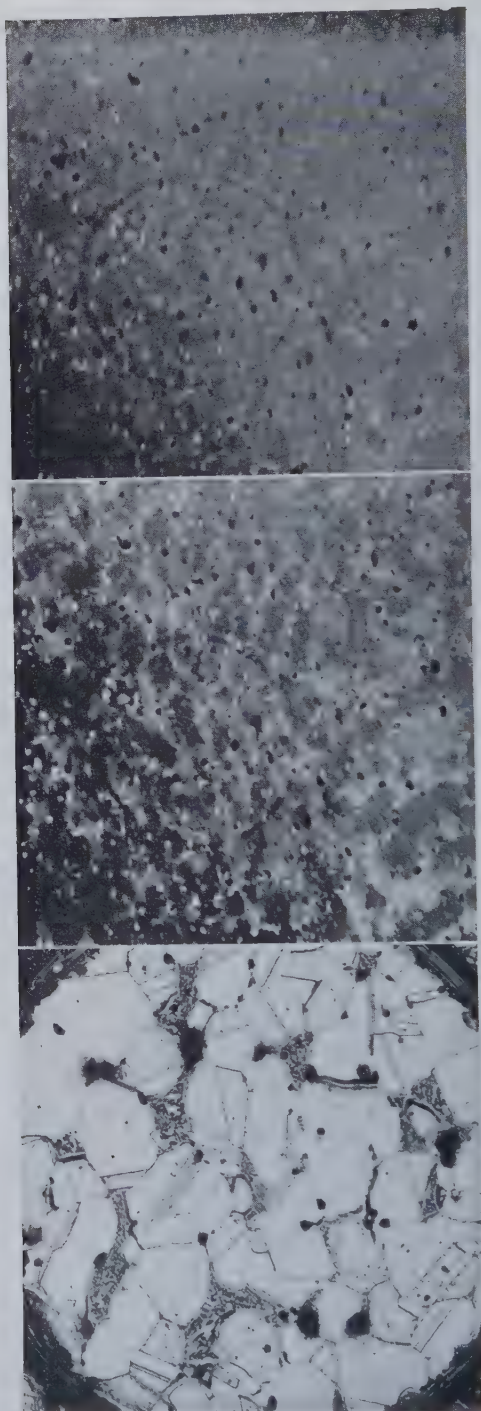


FIG. 9.—ALLOY 3 (COPPER-ZINC-TIN-LEAD).

$\times 200$.

- a. Photomicrograph showing alpha and gamma phases. $\times 200$.
 b. Radiograph: Cu radiation, 30 kv., $\times 100$. White dots, Pb; black dots, voids. Tin-rich material is light against darker copper-rich material.
 c. Radiograph: Mo radiation, 42 kv. $\times 100$. Same details as b but less contrast.

Original magnifications given; reduced approximately one third in reproduction.

is chosen so that no interference arises from the background peak. The values of $(\mu_2 - \mu_1)$ for both Mo K and Co K are negative so that Fe segregations in Cu,

in the radiograph. The distracting details of the brass grain structure were eliminated and the Fe particles were shown to be considerably elongated. This property

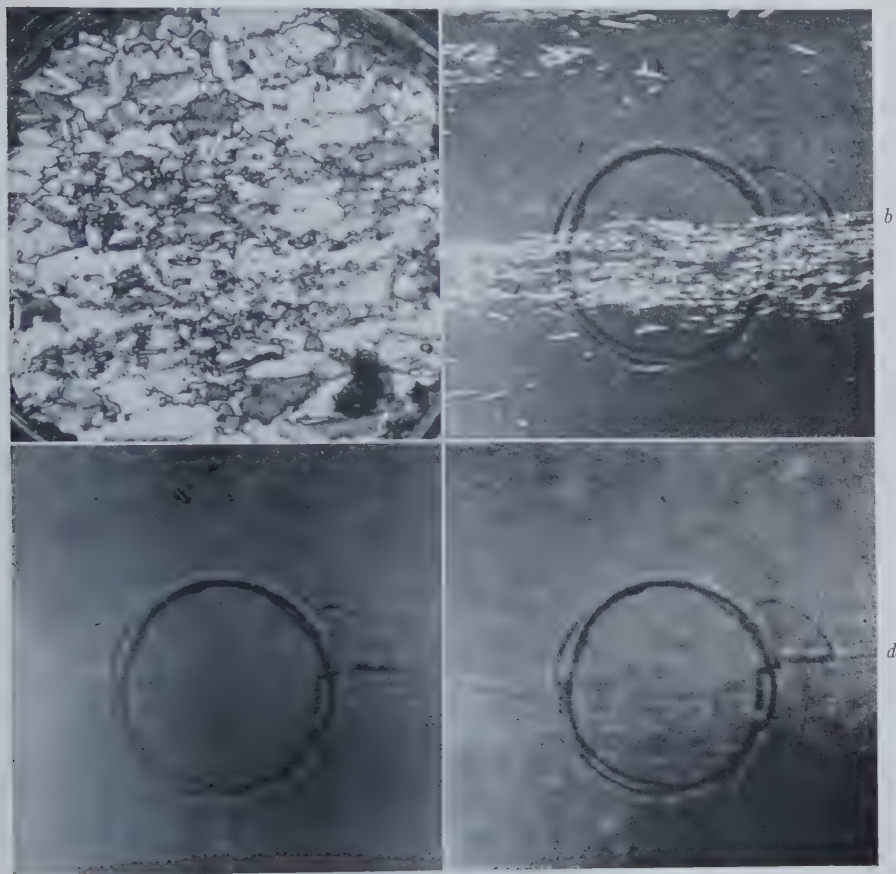


FIG. 10.—ALLOY 4 (COPPER-ZINC-IRON).

- a. Photomicrograph showing iron-rich particles. $\times 200$.
- b. Radiograph: Cu radiation, 30 kv. $\times 100$. Iron-rich particles are white.
- c. Radiograph: Mo radiation, 42 kv. $\times 100$. Iron-rich particles slightly darker than background.
- d. Radiograph: Co radiation, 30 kv. $\times 100$. Iron-rich particles slightly lighter than background.

Original magnifications given; reduced approximately one third in reproduction.

if revealed at all, would be dark against a lighter background which is the reverse of their appearance with Cu radiation.

Example 4 consisted of Cu-Zn-Fe in the hot-forged condition. Comparison of Figs. 10a and b demonstrates the clarity with which the Fe constituent was revealed

was not strongly emphasized in the photomicrograph. The high Fe content of the particles was clearly indicated by comparison of Figs. 10b and c taken with Cu and Mo radiations, respectively. In the former the particles were bright against a dark background while in the

latter they were very slightly darker than the background.

With Co radiation, particles still were slightly lighter than the background,

particles with Co radiation might be attributed to Mn. As shown in Table 2, if all existing Mn were dissolved in the Fe particles the value of $(\mu_2 - \mu_1)$ would

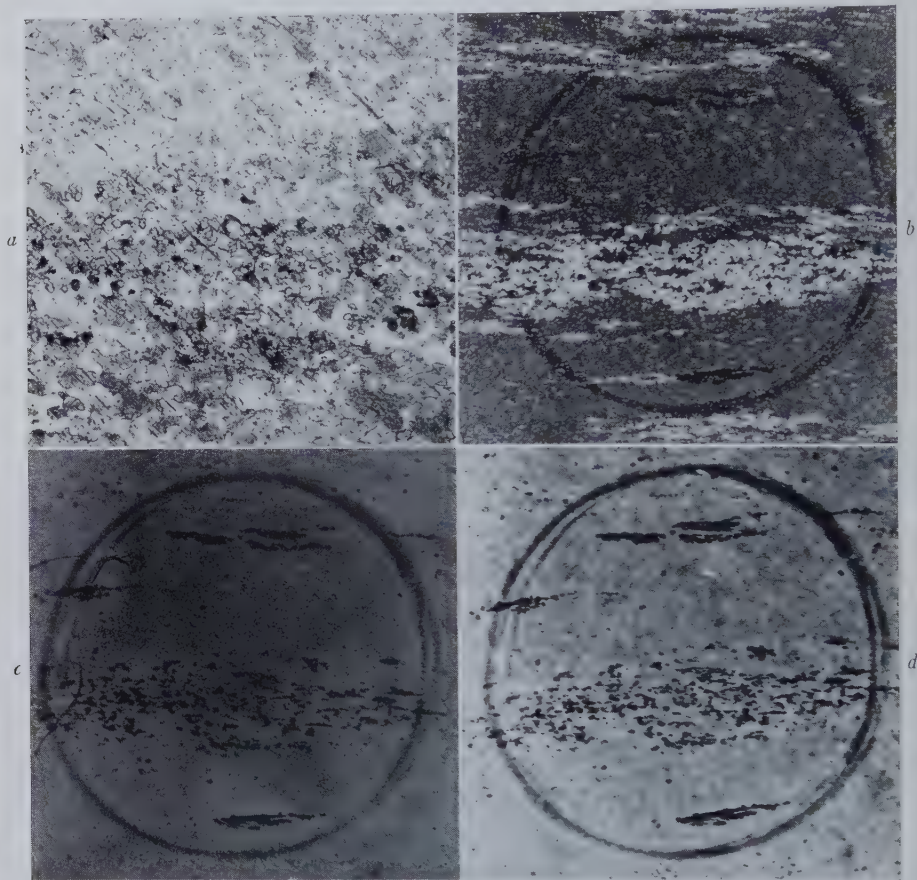


FIG. 11.—ALLOY 5 (COPPER-ZINC-IRON-TIN-SILICON).

- a. Microradiograph showing iron-rich particles. $\times 200$.
- b. Radiograph: Cu radiation, 30 kv. $\times 100$. Iron-rich particles are white, voids are black.
- c. Radiograph: Mo radiation, 42 kv. $\times 100$. Black dots may be FeSi.
- d. Radiograph: Co radiation, 30 kv. $\times 100$. Black dots may be FeSi.

Original magnifications given; reduced approximately one third in reproduction.

which on first consideration would not have been expected for pure Fe. The chemical analysis (Table 1) showed the presence of a small amount of Mn. As will be discussed later, Mn has a high positive absorption differential for both Cu and Co radiations (Fig. 14) and therefore a slight indication of the

still have been negative for Co $K\alpha$ radiation. However, an alloy of 90 per cent Fe, 10 per cent Mn would have a positive differential for Co $K\alpha$ radiation and a negative differential for Mo radiation. It could thus be suggested that the observed effect was produced by a highly localized distribution of Mn in the Fe particles,

which caused the concentration in some parts to reach a value as high as 90 per cent Fe and 10 per cent Mn.

Referring to Fig. 4, it will be noted that,

the composition Cu-Zn-Fe-Sn-Si. Again the iron-rich particles were clearly indicated as light against a dark background for Cu radiation, but for either Co or Mo

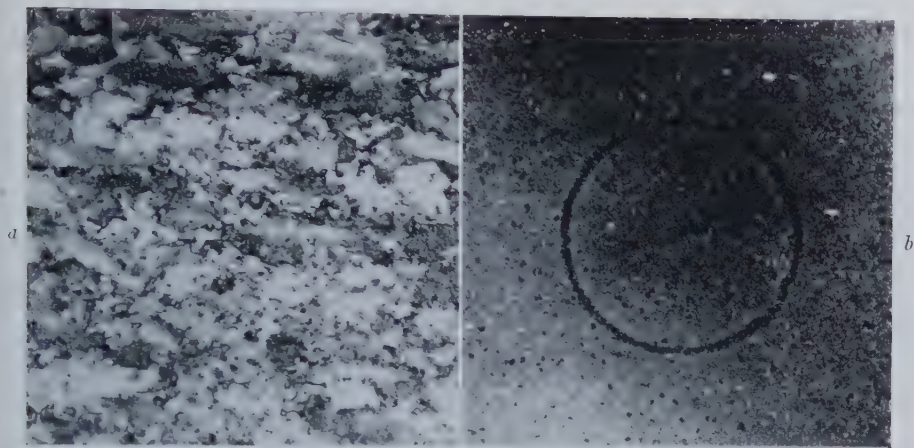


FIG. 12.—ALLOY 6 (COPPER-ZINC-TIN-ALUMINUM-IRON-MANGANESE).

a. Photomicrograph showing iron-rich particles. $\times 400$.

b. Radiograph: Cu radiation, 30 kv. $\times 100$. Iron-rich particles are white.

Original magnifications given; reduced approximately one third in reproduction.

whereas the Co $K\alpha$ radiation falls in a region where $(\mu_2 - \mu_1)$ is negative for Fe inclusions in a copper-base matrix, at the same time the Co $K\beta$ falls within the sensitive region of high positive values for $(\mu_2 - \mu_1)$. Thus, although the intensity ratio between β and α lines is only 0.175, nevertheless the high absorption differential for the β lines could readily cause the effect observed in the radiograph. We have already discussed an analogous case for one of the Sn alloys, in which case the background peak interfered with the results in a similar manner.

From the two examples already encountered, it can be seen that whenever paradoxical situations arise, involving very low contrast, a careful comparison should be made between the absorption differential curves and the X-ray emission curves before any final conclusions are reached.

A second example of an iron-containing alloy was examined in specimen 5 with

targets were either invisible or dark against a lighter background (Fig. 11*b*, *c* and *d*). The particles were small and equiaxed as compared with the elongated particles of the previous example. Although the magnification was lower than for the photomicrograph (Fig. 11*a*) the particles were much more clearly indicated than in the latter. The three-dimensional nature of the sample is strongly emphasized by the much greater apparent density of Fe particles in the micro-radiograph than in the photomicrograph.

In all three radiographs certain dark features occurred, but these seemed to be more numerous with Co and Mo radiations than with Cu. The elongated black streaks as well as some rounded black markings were visible with all three radiations and probably indicated voids. The small rounded black markings with Mo and Co radiations considerably outnumber those visible with Cu and many of them can be matched up with the

iron-rich particles seen in Fig. 11*b*. These were probably due to the presence of Si in the particles.

Other evidence has previously suggested the formation of an iron silicide when

being distributed among all of them as the solid solution. This agrees with the small number of dark spots in Figs. 11*c* and *d* compared with Fe particles in Fig. 11*b*.

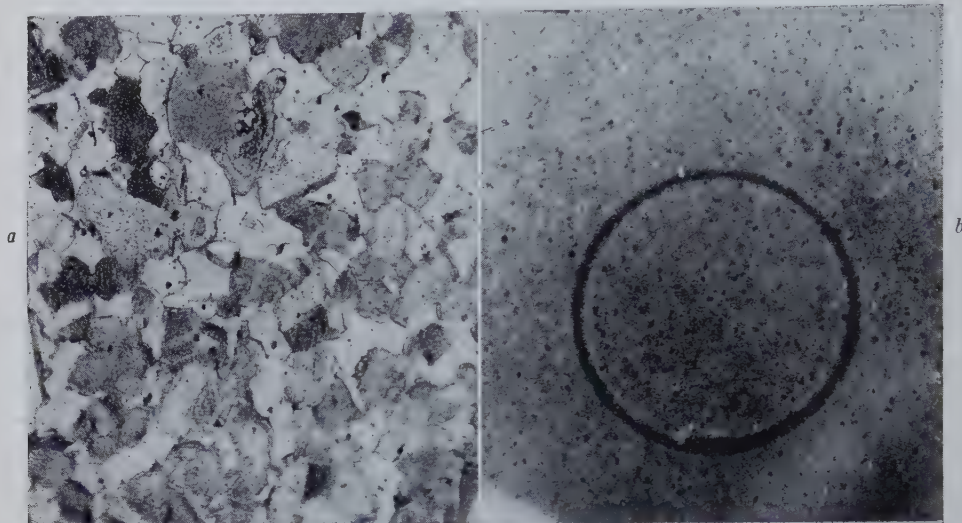


FIG. 13.—ALLOY 7 (COPPER-ZINC-TIN-IRON).

a. Photomicrograph showing iron-rich particles. $\times 400$.

b. Radiograph: Cu radiation, 30 kv. $\times 100$. Fe particles are white.

Fe and Si are both present in a brass. Fig. 4 shows that Fe has a small negative value of $(\mu_2 - \mu_1)$ for both Co and Mo radiations, but in other samples in our experience pure Fe particles have not been clearly visible with either of these radiations. Fig. 7 shows that either FeSi or FeSi₂ particles would satisfy the conditions; viz., a high positive value of $(\mu_2 - \mu_1)$ for Cu radiation, which would show them with high contrast as white on a dark background; negative values of the differential for both Co and Mo radiations, but with $|\mu_2 - \mu_1|$ considerably greater than for Fe particles so that the iron silicide should be visible as dark particles on a lighter background. Since the Si is present in small quantity, it would have to be concentrated in a few iron-rich particles as the silicide rather than

Specimens 6 and 7 (Figs. 12 and 13) are further examples in which the Fe distribution was extremely fine. Some of the details visible in the original enlargement negatives at 100 diameters were of the order of 0.1 mm. or less. The actual particles were about 10^{-4} cm. in diameter. This was particularly evident in specimen 7, where the Fe particles were not clearly resolved in the photomicrograph even at $400\times$ magnification.

For Fe in a Cu matrix the absorption differential $(\mu_2 - \mu_1)$ with Cu K-radiation is about 2000. For the brass under investigation the value would be somewhat less. Since equiaxed particles of 10^{-4} cm. in diameter are clearly distinguished, one obtains $(\mu_2 - \mu_1)l_2 = 2000 \times 0.0001 = 0.2$; or $I_2/I_1 = e^{-0.2} = 0.819$.

Thus a 20 per cent difference in transmitted intensity will readily reveal a

difference in composition unless sensitivity is reduced by interference from the background radiation. In the present example the detection of smaller particles was

Manganese in Copper Alloys

A similarity exists between these alloys and those containing Fe. Again the absorption differential curve (Fig. 14) possesses

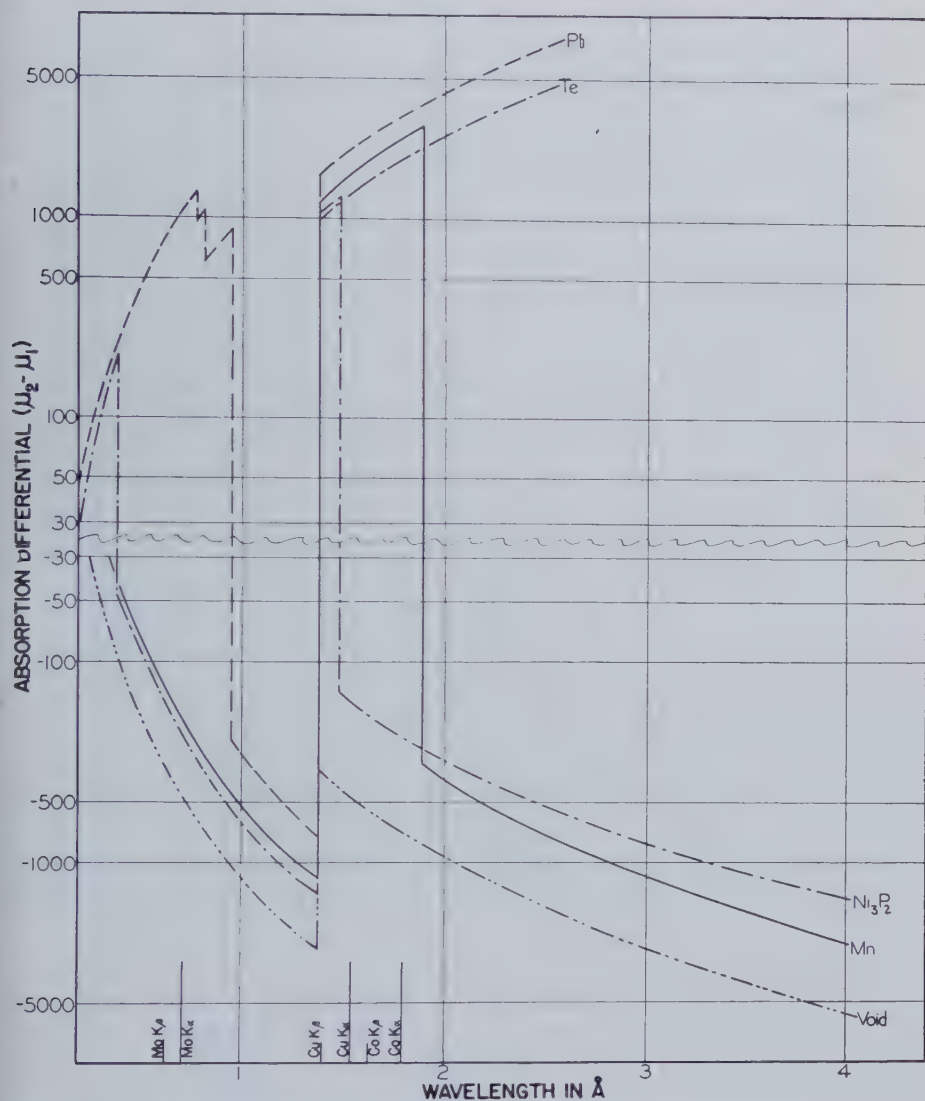


FIG. 14.—LINEAR ABSORPTION DIFFERENTIALS BETWEEN COPPER AND MANGANESE, TELLURIUM, NICKEL PHOSPHIDE AND LEAD.

Te and Ni_3P_2 curves superimposed below $1.37 \text{ \AA}$.

probably limited by the magnification so that for larger inclusions a still smaller value of I_2/I_1 would be satisfactory.

a highly sensitive band containing in this case the wave lengths of both Cu K and Co K but not that of Mo K. Strong con-

trast would result for Mn segregations inspected with either Cu or Co targets, but no detail would be observed with Mo radiation or with Fe or Cr targets if the latter were available.

cipitate, as indicated by the white particles revealed by Co radiation (Fig. 15*c*) but not by Mo radiation (Fig. 15*d*). By comparison of Figs. 15*b* and *c*, it can be seen that the contrast was much greater with

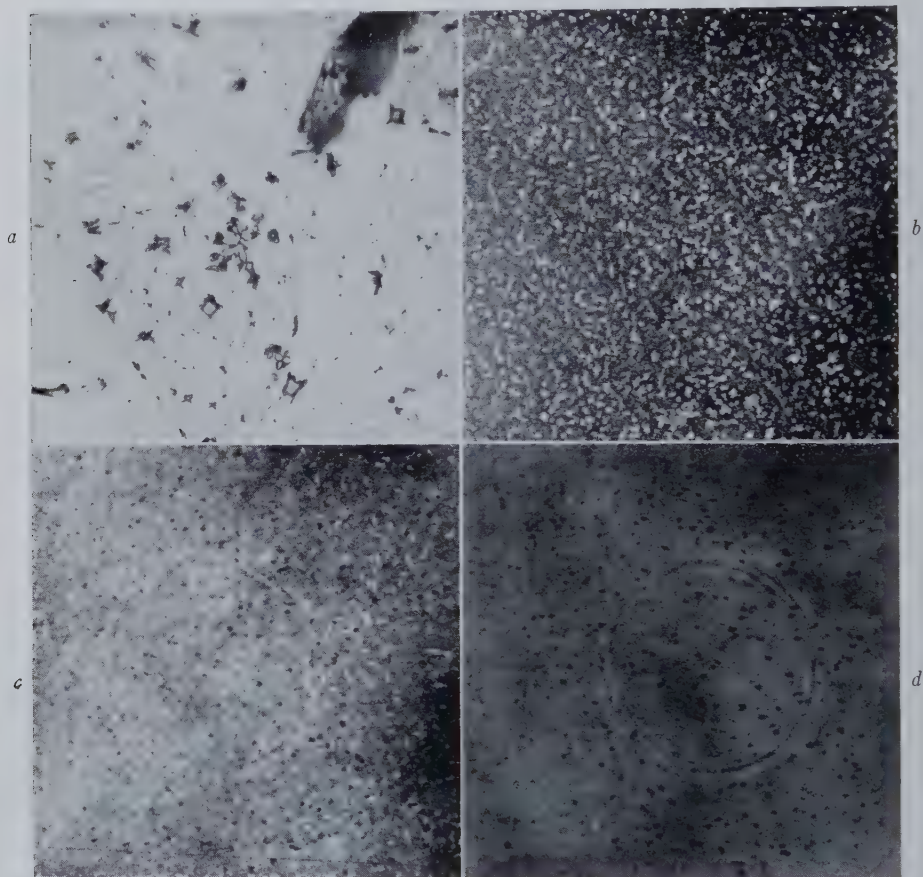


FIG. 15.—ALLOY 8 (COPPER-ZINC-ALUMINUM-MANGANESE-IRON).

- a.* Photomicrograph showing Mn-Fe particles. $\times 400$.
- b.* Radiograph: Cu radiation, 30 kv. $\times 100$. Mn-Fe particles are white.
- c.* Radiograph: Co radiation, 30 kv. $\times 100$. Mn-rich particles are white.
- d.* Radiograph: Mo radiation, 42 kv. $\times 100$. Voids darker than background; no trace of Fe or Mn.

Original magnifications given; reduced approximately one third in reproduction.

Sample 8 was a manganese bronze, containing both Mn and Fe, with segregated particles as shown in Fig. 15*a*. Mn in this quantity would be in solid solution in Cu. In the present alloy, however, Mn was contained in the pre-

a Cu target than with the Co target although the absorption differential curve for Mn vs. Cu has a considerably lower value for Cu rays than for Co. This indicates that Fe is also present in the segregated particles.

Lead in Copper Alloys

The presence of Pb has already been indicated for previous examples. The absorption differential for Pb vs. Cu is

low power before etching, this specimen seemed to have streaks parallel to the working direction. It was found extremely difficult to etch the specimen without

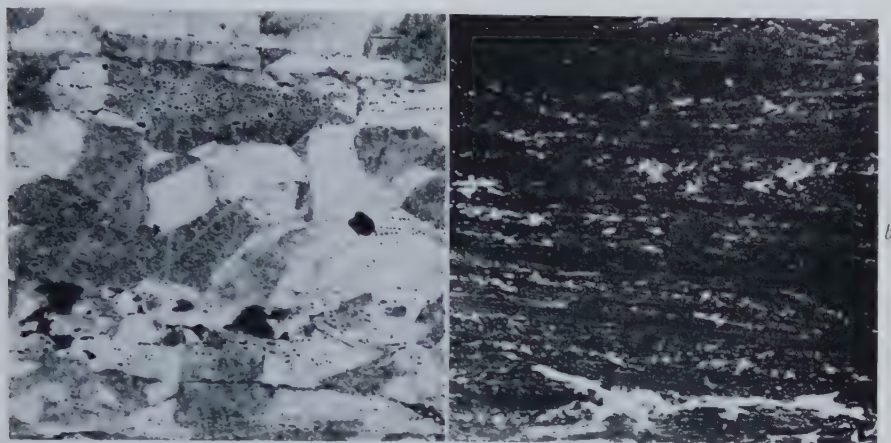


FIG. 16.—ALLOY 9, LEADED BRASS.

a. Photomicrograph showing Pb distribution. $\times 150$.

b. Radiograph: Cu radiation, 30 kv. $\times 100$. Pb is white.

Original magnifications given; reduced approximately one third in reproduction.

everywhere positive except in a rather narrow region of wave lengths just short of the Cu K absorption limit (Fig. 14). Thus, for almost any target, Pb will be shown as white on a dark background. Since the value of $(\mu_2 - \mu_1)$ is quite high, minute particles can be detected.

A specimen of cold-drawn leaded brass was chosen as specimen 9. Figs. 16a and b demonstrate the appearance of Pb in a photomicrograph and in a radiograph. The shape of the Pb particles indicated in the photomicrograph was by no means a true picture; instead of the more or less rounded appearance shown under the microscope, the Pb particles were actually greatly elongated in the direction of working of the metal. The optical picture apparently represented the cut made by the plane of polish through various projections and irregularities in the Pb stringers.

An interesting example of a leaded alloy was contained in specimen 10, which was a leaded silicon bronze. When examined at

etching out the particles contained in the streaks. The particles were suspected of containing Pb but the etching properties were similar to neither Pb nor the silicon-rich particles found in ordinary silicon bronze. Under radiographic examination these particles showed sharply white with all three radiations as indicated in Fig. 17. However, the contrast was less strong with Mo radiation, which suggested a possible compound containing Pb and Si. Unfortunately, since the absorption differential is negative for Si vs. Cu for all radiations and is positive for Pb vs. Cu for most radiations, it was impossible to prove definitely whether or not such a compound existed.

Tellurium in Copper Alloys

The alloys of Cu containing Te have recently received considerable attention. Te vs. Cu has high positive values of the absorption differential for both Co and Cu radiations and a much smaller negative

value for Mo radiation. Te or a copper telluride should therefore appear white against a dark background with the former radiations, but would probably not be visible with Mo.

to the telluride, one may expect to encounter a precipitated nickel phosphide such as Ni_3P_2 or Ni_5P_2 . It would be desirable to distinguish between these compounds and this is difficult to do by

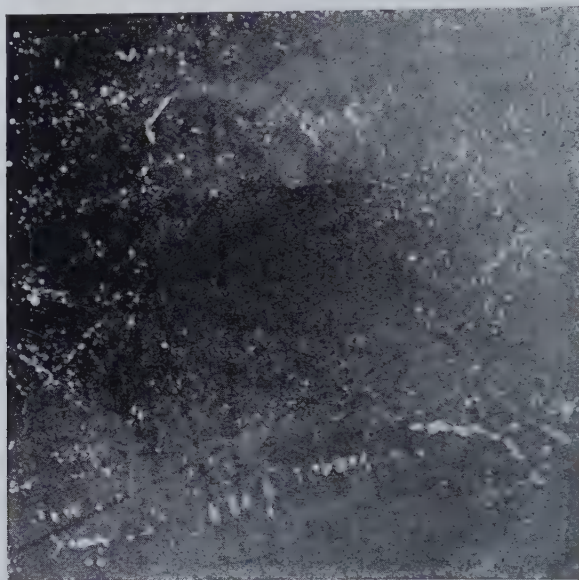


FIG. 17.—ALLOY 10, LEADED SILICON BRONZE.

Radiograph: Cu radiation, 30 kv. $\times 100$. Lead-rich particles are light against darker background. Some particles have lower contrast than expected for Pb (Pb-Si?)
Original magnifications given; reduced approximately one third in reproduction.

Specimen 11 was a defective sample of Cu containing Te. According to the photomicrograph of Fig. 18a, the Te was segregated in small rounded particles, but the radiograph (Fig. 18b) showed that the particles actually were elongated into broken stringers. Fig. 18c shows the same material after an anneal in hydrogen at 815°C . The grain structure seemed to have opened up and the Te was now concentrated in rounded globules; a change that was not evident in microscopic inspection.

A more complex Te alloy containing also Ni and P was chosen for example 12. Fig. 19a is a photomicrograph of this alloy in the extruded condition showing elongated inclusions as well as grain-boundary films. In this alloy, in addition

microscopic methods. As shown in Fig. 14, the absorption differential for Ni_3P_2 vs. Cu is always negative except in an extremely narrow range between the K absorption limits of Ni and Cu. For all other wave lengths the phosphide will appear dark against a light background and the particles will be distinguishable from voids only by a judgment of the contrast or by close matching with a photomicrograph.

The only strong radiations with wave lengths in the narrow band of positive differential are the Zn K, W L, or Os L. Unfortunately, as shown in Fig. 14, even in this region conditions are not very favorable, since the Ni_3P_2 curve is almost superimposed on that of Te for all wave lengths below $1.48 \text{ \AA}$. Granted that the curve for a copper telluride would be



FIG. 18.—ALLOY 11, DEFECTIVE COPPER-TELLURIUM ALLOY.

a. Photomicrograph at fracture showing round telluride particles. $\times 250$.

b. Radiograph: Cu radiation, 30 kv. $\times 100$. Telluride stringers lighter than background.

c. Radiograph: Cu radiation, 30 kv. $\times 125$. Same material as *b* after hydrogen anneal showing spheroidized telluride (white) and open grain boundaries (black).

Original magnifications given; reduced approximately one third in reproduction.

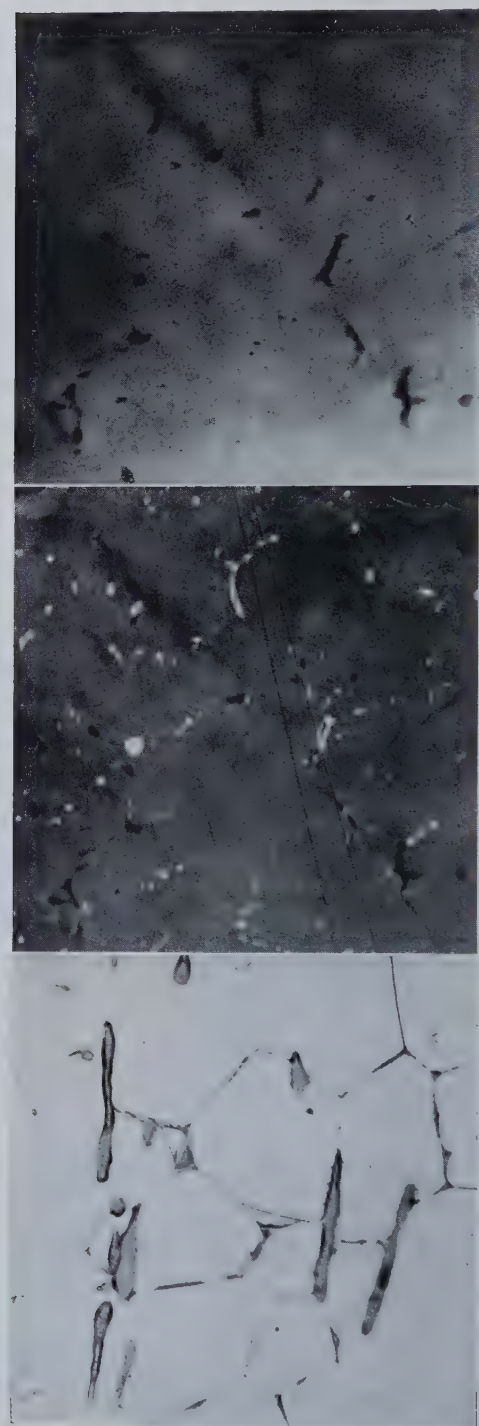


FIG. 19.—ALLOY 12 (COPPER-ZINC-NICKEL-TELLURIUM-PHOSPHORUS).

- a.* Photomicrograph showing grain-boundary films and elongated particles of either telluride or phosphide. $\times 500$.
b. Radiograph: Cu radiation, 30 kv. $\times 100$. Cu_2Te is white, voids are dark. Nickel phosphide not visible.
c. Radiograph: Mo radiation 42 kv. $\times 100$. Voids are black, telluride and phosphide not visible.
 Original magnifications given; reduced approximately one third in reproduction.

somewhat lower than the displayed curve, nevertheless the difference in contrast between telluride and phosphide would not be great.

match between radiographs with Cu radiation and either Zn K or W L radiations as well as with the photomicrograph. Such radiations were not at present



FIG. 20.—ALLOY 13 (COPPER-ZINC-NICKEL-TELLURIUM-PHOSPHORUS).

a. Photomicrograph showing broken stringer of precipitate. $\times 200$.

b. Radiograph: Cu radiation, 30 kv. $\times 100$. White discontinuous stringers of telluride. Original magnifications given; reduced approximately one third in reproduction.

In Figs. 19*b* and *c* are shown radiographs of this alloy with Cu and Mo radiations (the radiographs are out of alignment with the photomicrograph by about 45°). In Fig. 19*b* most of the white particles (telluride) are shown to vaguely follow the grain outlines although some correspond to the elongated particles of Fig. 19*a*. In addition, a number of dark features may be observed, also mainly in grain boundaries. These might be presumed to be the phosphide.

With Mo radiation, however, both telluride and phosphide should appear dark on a lighter background and for particles of the same size should have nearly the same contrast. Fig. 19*c* for the Mo target shows no dark features to match the white details (telluride) on Fig. 19*b*. Therefore the dark features seen in both of these microradiographs were probably voids.

In order to detect the nickel phosphide, it would be necessary to make a close

available in this laboratory; our facilities are being extended at the present time.

A second sample of this alloy (specimen 13) was examined after cold-working. In the photomicrograph (Fig. 20*a*) it was observed that the elongated inclusions were sometimes broken up into discrete particles by the cold-work. This was at first assumed to be a preferential etching effect. However, as shown in the radiograph (Fig. 20*b*) this condition was common to most of the inclusions. Since the majority of these were buried beneath the etched surface, the condition was thus shown to be truly a result of cold-work rather than of the etching technique.

IDENTIFICATION OF UNKNOWN CONSTITUENTS

The properties of the microradiographic technique explained and illustrated in the preceding sections may on occasion be used to identify the composition of unknown segregations or inclusions.

Example 14 was a chill-cast sample of 70-30 brass containing minute interdendritic cavities. Figs. 21*a* and *b* are radiographs with Cu and Co targets,

would also produce the same effect (Fig. 5). Thus it was suggested that the particles were an Fe-Mn alloy, since this would be a reasonable combination. One of the largest

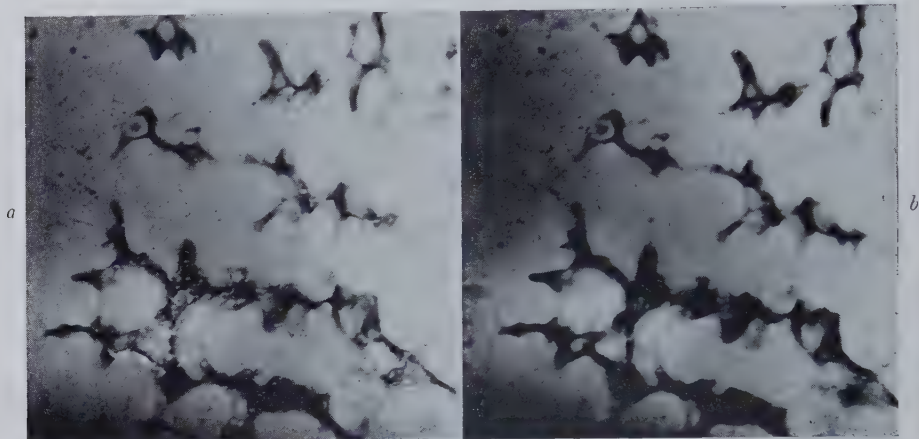


FIG. 21.—ALLOY 14. RADIOGRAPHS OF CHILL-CAST CARTRIDGE BRASS SHOWING FILMS OF IRON-RICH IMPURITIES.

a. Cu radiation, 30 kv. $\times 100$. Fe is white, voids are black.

b. Co radiation, 30 kv. $\times 100$. No trace of Fe films.

Original magnifications given; reduced approximately one third in reproduction.

respectively. The former revealed films of impurities deposited in the cavities (white features) but these were not shown by Co radiation. From the information in Figs. 4, 5 and 14, it can be deduced that Fe was contained in the films.

Example 15 was a sample of 90-10 brass that had been subjected to a swaging operation. Subsequent machining revealed a number of isolated groups of inclusions, which could be seen under a low-power microscope. Figs. 22*a*, *b* and *c* are radiographs taken with Cu, Co and Mo radiations. A high positive value of $(\mu_2 - \mu_1)$ was found for Cu, a much lower positive value for Co and a negative value for Mo radiation. Previous discussions of Fe inclusions suggest at once that these particles contained Fe, but a particle of pure Fe would not have a strong positive absorption differential for Co radiation. However, if some Mn were also present, the effect would be exactly that found here; elements between Nos. 42 and 60

particles (about 0.1 mm. diameter) was isolated under a low-power microscope and when examined by X-ray diffraction gave the characteristic pattern of Fe. This corroborated the radiographic results. The ambiguity regarding the second element could have been removed if additional radiations had been available. Because of the widely separated condition of the inclusions, spectrographic analysis of the alloy did not indicate their composition.

Further information was also deduced from the radiograph. If the particles had been present previous to the swaging operation, the group should be extended in the direction of the metal flow. Since they were grouped in a rough circle, it was suggested that the particles had been introduced during or subsequent to the swaging procedure.

SUMMARY AND CONCLUSIONS

The microradiographic technique has been described and a discussion presented



FIG. 22.—ALLOY 15. RADIOGRAPHS OF SWAGED 90 PER CENT COPPER, 10 PER CENT ZINC CONTAINING INCLUSIONS OF IRON ALLOY (POSSIBLY IRON-MANGANESE). $\times 100$.

a. Cu radiation, 30 kv. Iron-rich inclusions are white.
 b. Co radiation, 30 kv. Iron-rich particles lighter than background (Fe-Mn?).
 c. Mo radiation, 42 kv. Black marks are voids. Fe particles not visible.
 Original magnifications given; reduced approximately one third in reproduction.

of the basic laws of X-ray absorption upon which the method depends.

A description has been given of the use of characteristic radiations of intermediate wave length and it has been shown that high sensitivity can be obtained in this manner.

A number of examples have been discussed, which indicate that the micro-radiographic method can serve as a powerful auxiliary to the metallographic microscope. Cases have been cited in which the radiograph revealed that the true shape of inclusions was different from that indicated by photomicrographs. Notable among these examples were the cases of Pb in cold-worked brass and Te in a cold-worked Cu-Te alloy. The choice of target element for maximum sensitivity in such cases depended upon the elements present in both matrix and inclusions.

A still more valuable use for the new tool lies in the determination of the distribution of elements in multiphase alloys. Since the phase diagrams for most of the examples were well known, it could be seen that the distribution of elements indicated in the radiograph was well substantiated by prior knowledge concerning the phases. For the explanation of these results, a detailed explanation of the absorption differential curves was necessary.

From the results described, the step to further applications of the method is obvious. If a considerable number of different radiations were available it is evident that the element distribution in complex alloys could readily be determined. This should be of assistance in the study of ternary, quaternary, and even more complex alloys.

In the present investigation only three radiations were available, so that the full power of the method in this direction could not be exploited. However, provision is being made for additional radiations and

it is expected that further interesting examples will be presented in the future.

It must be emphasized that, for full value in the detection of the distribution of the elements, careful attention must be given to the operating voltage as well as to the choice of target element. For this purpose a study of the absorption differential curves is necessary for each individual case.

ACKNOWLEDGMENT

Thanks are due the Chase Brass and Copper Co. for permission to publish this work. The interest and encouragement of Dr. D. K. Crampton are gratefully acknowledged, as well as the interest of other members of the Research Department who made possible the collection of some of the specimens investigated. The assistance of Mr. H. W. Hughson in preparation of the photomicrographs and other details of the photographic work is deeply appreciated.

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ADDENDUM

It should be noticed in Fig. 4 that the beta line for Co falls within the highly sensitive band for Fe in Cu alloys. However, the intensity of the beta line is only about one fifth that of the alpha line. As a result, for small Fe particles the disturbing effect of the beta line is not serious, and the particles are almost completely invisible with Co radiation as indicated in the paper. For large Fe particles, however, the absorption effect on the beta line is sufficient to reveal the particles with appreciable contrast. This effect was neglected in the paper in Figs. 15-c and 22-b. When these radiographs were repeated with Co radiation from which

the beta line had been eliminated by filtration, the particles of Fig. 15-c showed only faintly, indicating a small trace of Mn but not the large amount first indicated in the discussion of this figure; the inclusions shown in Fig. 22-b became slightly darker than the background, indicating that the particles were Fe without any trace of Mn.

DISCUSSION

(Robert Treuting presiding)

T. A. READ,* Philadelphia, Pa.—Dr. Maddigan, can you assume how much more it would be possible to increase the resolution you can get by this method? What are the limiting factors?

S. E. MADDIGAN.—In regard to the size of particles or contrast?

T. A. READ.—Size of particles.

S. E. MADDIGAN.—I think the resolution depends entirely on grain size of the radiographic plates. With the present Eastman 548-o spectrographic plates (500 lines per millimeter), without using extreme care in the processing, 100 diameters is the limit of magnification. With extreme care, however, and with all conditions favorable, it is possible to go as high as 400 diameters. However, the emulsion is not completely uniform, so that, even with a well standardized procedure, many radiographs will not be capable of 400 diameters magnification. For a great many purposes 100 diameters or less is all that is required, and with reasonable care this magnification can be attained 100 per cent of the time.

F. N. RHINES,† Pittsburgh, Pa.—I should like to ask Doctor Maddigan two questions: first, would it be possible to so calibrate the method that one might read the composition at a specific point within a cored solid solution; second, is there any possibility that one could distinguish alpha and beta in manganese bronze in the alpha-beta range?

S. E. MADDIGAN.—I will answer Dr. Rhines' second question first. The question of distinguishing between alpha and beta depends, of course, on the relative solubility of the manganese in the two phases. I believe this could be done because, in the present alloy, which had not been homogenized to any extent, we could faintly distinguish between alpha grains themselves due to slight variations in the manganese content. This was in pictures taken with filtered cobalt radiation, where the disturbing effect of the small iron-rich particles was minimized. Of course, in the pictures where the field is crowded with small particles showing with high contrast, it is rather hard to distinguish any slight variations in the background of the matrix.

With regard to the final determination of composition of the particles, we found that using cobalt-filtered radiation the particles were still visible, but with only slight contrast. In other words, the manganese content of the iron-rich particles is slightly greater than that of the matrix, but not nearly as high as we had at first interpreted it.

The quantitative determination of composition at a specific point in the field would, of course, involve densitometer measurements and I think this could be carried out in a semiquantitative fashion, but without any high degree of accuracy. The method is extremely sensitive to small variations in composition, particularly for elements such as tin. In any case, where the sensitivity is high because of high values of the absorption differential, variations involving only low percentages of the minor element could be detected with a fair degree of accuracy. However, where one encounters large amounts of the given element, then one would be working with one phase on the upper flat region of the photographic exposure curve, where there would be little change in contrast for a large change in composition. Since one has to work with a contrast between the matrix and the secondary phase, it is not possible here to make a free choice of the region of the photographic curve such as may be done in some types of intensity work.

Suppose, for instance, one had a particle that was light against a dark background, the background being so black as to be on the upper flat part of the photographic curve.

* Ordnance Laboratory, Frankford Arsenal.

† Department of Metallurgy, Carnegie Institute of Technology.

One could decrease the exposure so as to bring the background down onto a more sensitive region of the photographic curve, but then the particles themselves would be so underexposed that again the accuracy would be poor. Under certain conditions, however, the method could be used successfully, and it is possible that by a proper choice of radiation one could normally cause both phases to fall on the sensitive straight-line portion of the photographic curve, where intensity measurements usually are made. However, I do not believe that high precision could ever be attained unless it were possible to adapt the microradiographic method to the use of Geiger counters.

L. FERGUSON,* New York, N. Y.—I think you said that the specimens used should be as thin as possible. I should like to know the thickness of the specimens you used for your illustrations. I should also like to know whether the specimen does not have to be highly polished, at least comparable to that done for ordinary microscopic examinations.

Another question also comes to my mind. You have two surfaces, a front surface and a rear surface. Do these surfaces have to be parallel? Some of your illustrations, for instance, look as though there is more exposure, or more light, in one corner than in another. Is that because the specimen was wedge-shaped rather than having parallel surfaces?

S. E. MADDIGAN.—The thickness of the specimens is controlled to some extent by the absorption coefficient of the matrix material and by the exposure time required. For copper alloys, most of our specimens are between 0.005 and 0.002 in. thick. These thicknesses were readily attainable. Because of the time requirements, no description of the experimental conditions was given in the oral presentation. However, brief details are given in the printed version and also in several of the references. The polish needs to be fairly good in order to avoid the deleterious effect of scratches appearing on the radiograph, but the radiographs are not as sensitive to surface scratches as a photomicrograph would be at the same magnification.

In regard to the question of whether the surfaces should be parallel, that depends on personal preference. We have frequently polished our specimens slightly wedge-shaped because this allows more latitude in exposure time. Thus while one part of our radiograph may be slightly off the optimum exposure time, another region where the specimen thickness is slightly different will be found to have the optimum exposure. Thus the number of exposures required to produce suitable results is reduced. As a matter of fact, some of the specimens shown here were made somewhat wedge-shaped for that reason. Perhaps these do not look so satisfactory when presented to an audience, but actually they are better for general use. It must be remembered in this regard that the useful range of the photographic plate is much greater than is that of the printing paper. Thus, regions that may appear hopelessly blackened in the print actually show considerable useful detail in the enlargement plate.

There is no great difficulty in polishing a specimen so that it is quite flat and uniform in gauge if that is desired. One must start, of course, with a sample that has been cut flat and generally uniform in thickness, such as can be obtained by using a bandsaw with a suitable guide. The important step is to have the specimen in its Lucite mounting properly aligned in the lathe so that it is turned down uniformly to the 0.010-in. stage. From this point it is quite easy to maintain the uniformity during the hand polishing. If one is dealing with a magnetic material such as a steel, I understand that the whole process down to the hand-polishing stage can be done on a magnetic grinder (personal communication from Dr. H. T. Clark of Jones and Laughlin Steel Corporation).

MEMBER.—With a photomicrograph, do you not obtain the same results in regard to the determination of shape, inasmuch as stringers are normal to the path of the beam you are projecting; and you can also see them as circular sections? Also, is a stereoscope possible for a deep specimen? Will it enable you to see in depth, instead of summing up the complete thickness of the sample in a single plane?

* Bell Telephone Laboratories.

S. E. MADDIGAN.—Clark, of the University of Illinois, has published a note regarding stereoscopic work, but I do not know what results he has had to date. I believe a stereoscope would be just as valuable for this purpose as in large-scale radiography.

In comparing the use of microradiography and photomicrography for the determination of the true shape of stringers, it is possible, of course, to obtain the true shape by the latter method, provided that the specimen is very carefully cut parallel to the stringer axis and at the same time one is fortunate enough to cut exactly through one or more of the stringers. On the whole, I believe the chances of obtaining a true picture are much better with the three-dimensional microradiograph than they are with a two-dimensional photomicrograph. Suppose, for instance, the surface is cut 15° or 20° off the stringer axis, and for simplicity let us assume that the stringers are long, slender cylinders. With the radiograph one still sees the full-length stringer, but foreshortened somewhat by viewing at 70° instead of 90° to the stringer axis. The photomicrograph, on the other hand,

shows only a cut through the cylinder, which will result in an elliptical section. Where the stringers are quite irregular, as in the leaded brass shown in Fig. 16, it can be seen that the plane in the photomicrograph will in many cases cut projections from the main body of the stringer rather than cut the main stringer itself, and this may give an entirely false impression of the stringer shape.

D. W. SMITH,* New Kensington, Pa.—This paper, coming at this time, will prove invaluable to others who may find microradiography useful in supplementing microscopic examinations.

In regard to stereoscopic microradiography, I might mention that we have had a little experience with this in our Laboratories in connection with studies on spot welds in aluminum alloys. When the pairs of stereoscopic radiographs are viewed by some suitable means, a three-dimensional effect is obtained, which appears to give a better impression of the shape of constituents or voids than does a single microradiograph.

* Aluminum Research Laboratories.

Metallography with the Electron Microscope

BY CHARLES S. BARRETT,* MEMBER A.I.M.E.

(Chicago Meeting, October 1943)

THIS paper is a progress report covering metallographic applications of the electron microscope that have been made during the past year at Carnegie Institute of Technology. An account is presented of the techniques that have been most satisfactory, the difficulties encountered, the resolution obtained, and the peculiarities that have been noted in the microstructures. About 1200 exposures have been made during the year on the instrument, which is an RCA type B2 transmission microscope,¹ and a number of these have been selected to illustrate the results obtained. Prints are also included showing the common types of falsities—to borrow a term from the biological field, the “artifacts.” In brief, the paper is a record of our attempt to determine the value of the electron microscope in the study of the structure of metals and alloys.

In addition to comments on techniques and the quality of photomicrographs obtainable with them, the paper discusses the nature of the etch attack on a few metals, and the possible relation between the fine structure revealed by etching and the mosaic block structure of the grains. Since numerous papers and reviews are available on the subject of imperfection in crystals, the comments here may be very brief; in fact, are restricted almost entirely to points having to do with recent theories relating the strength of metals

to imperfections and to spacings of slip lines.

SPECIMEN PREPARATION AND PHOTOGRAPHS

Mechanical polishing by hand was used throughout this work. Precautions that must be taken in microscopy at high magnification, which have been well explained by Vilella in his book on Metallographic Technique for Steel, are likewise important with the electron microscope. This applies particularly to the need for repeated polishing and etching (each successive polish becoming less severe and each etch lighter), since the final etch should in general be no heavier than is used for oil-immersion optical microscopy and in many instances should be much lighter (compare Figs. 6*a* and 7*a*, 6*d* and 7*b*). An extremely light etch, of course, is incapable of cutting through a flowed layer of appreciable thickness. Unquestionably it would be very advantageous in each instance to compare the structures obtained by electrolytic polishing with those obtained by mechanical polishing, but difficulties with the electrolytic method have prevented this in the following collection of prints. The choice of etchant is important, of course; for example, picral proved superior to nital for tempered martensite.

With the exception of Figs. 1*b* and 1*c*, the replicas used were of silica, deposited upon polystyrene and floated from the polystyrene in ethyl bromide according to the method of Heidenreich and Peck.² The samples were mounted in Bakelite, polished and etched, then the polished Bakelite

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* Member of Staff of the Metals Research Laboratory and Associate Professor of Metallurgy at Carnegie Institute of Technology, Pittsburgh, Pennsylvania.

¹ References are at the end of the paper

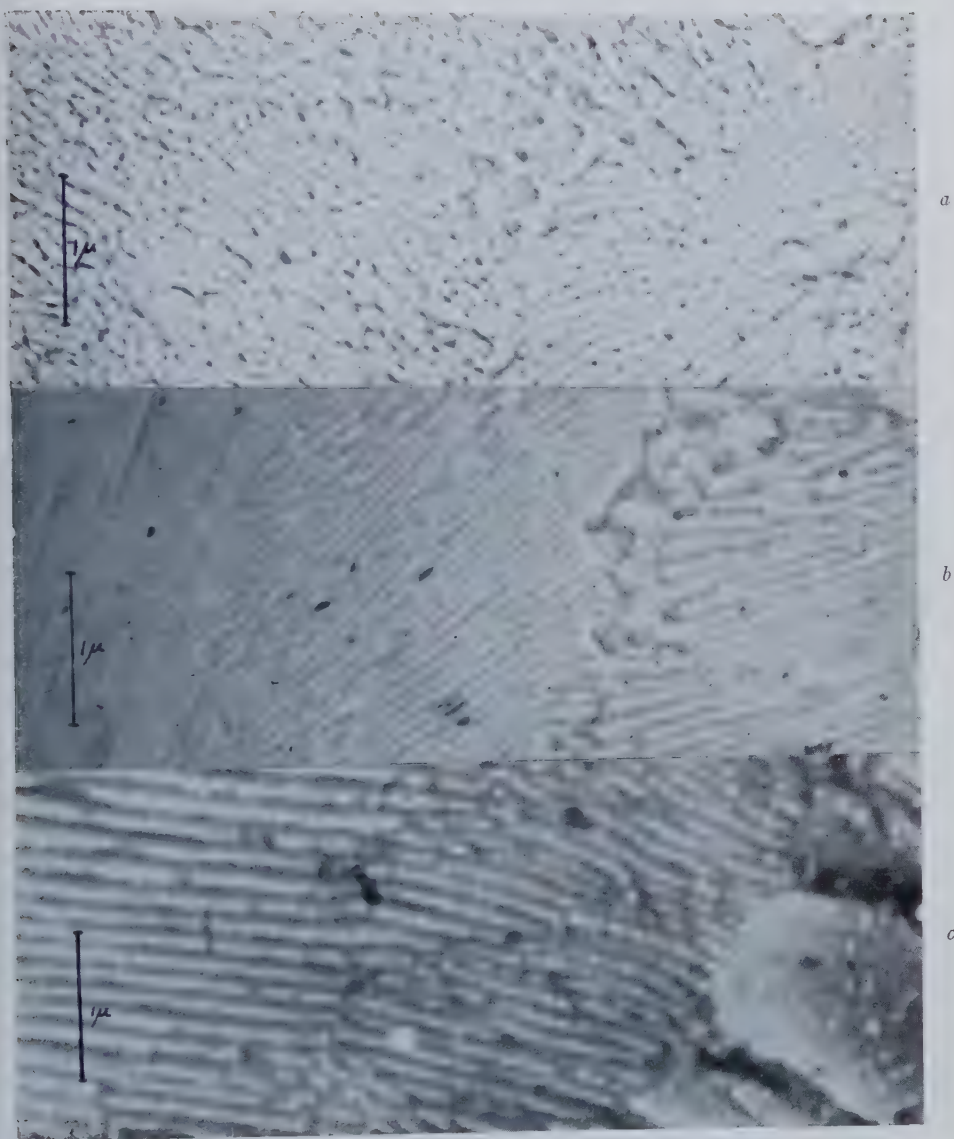


FIG. 1.—PEARLITE IN QUENCHED EUTECTOID STEEL. $\times 20,000$.
a. Polystyrene-silica replica.
b. Formvar replica, wet stripping.
c. Formvar replica, scotch tape stripping separated under xylol. Picral etch.

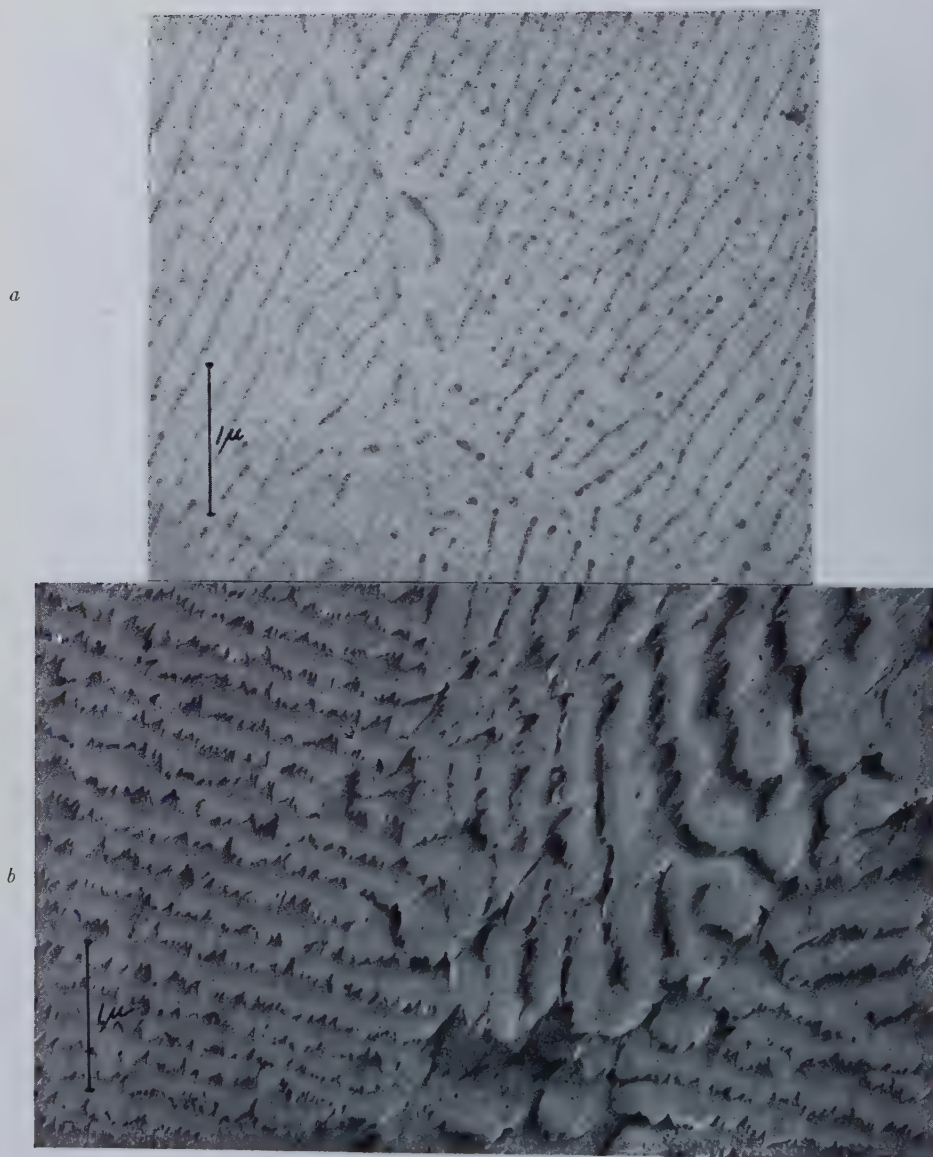


FIG. 2.—PEARLITE IN EUTECTOID STEEL. $\times 20,000$.

a. Etched in boiling sodium picrate for 10 minutes.

b. Etched in 0.5 per cent nital for 1 minute; cementite lamella nearly parallel to surface.

surface was given a very slight coat of beeswax in ethyl bromide and placed in a mounting press under powdered polystyrene. The press was heated to 150°C.

that a batch of polystyrene that had been stored in its cardboard container for a year was much more likely to stain than was a fresh batch. Staining was avoided by mold-

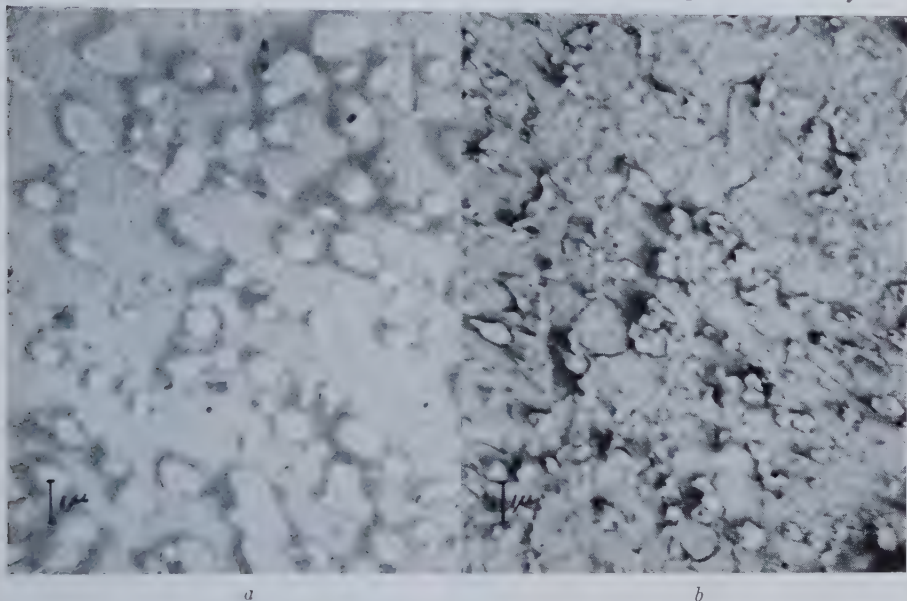


FIG. 3.—SPHEROIDIZED STEEL. PICRAL ETCH. $\times 5000$.

a. 0.60 per cent carbon steel, spheroidized 8 hours at 650°C.

b. Low-alloy steel, quenched from 1650°F., tempered 3 hours at 480°C., spheroidized 23 hours at 775°C.

before applying pressure, then cooled to 70°C. while under a constant pressure of 3000 lb. per sq. in. The Bakelite-polystyrene interface then cleaved apart very easily, exposing the molded replica of the specimen surface, on which the silica was deposited from a tungsten conical filament in a small chamber evacuated by an oil diffusion pump. The distance from filament to specimen was 13 cm. and care was taken to avoid overheating the polystyrene surface; heating times of 30 sec. were normal and it was found best to do the entire evaporation at one heating.

Unless the specimen is thoroughly washed after etching there is likely to be an additional etching or a staining of the specimen during the molding operation. Fig. 13*b* illustrates the effect, and Fig. 13*d* may also be related to it. It was also noted

ing in lucite, but difficulties were encountered in removing the silica replica from lucite. "Polystyrene lines," which characterize incomplete cleavage of the plastic from the specimen, are readily recognized (Figs. 12*a* and 12*b*) and these areas may be avoided easily in the final photography. It was felt that defective cleavages were so rare and so easily recognized that it was not worth while to resort to the more laborious method of etching the sample away from the specimen.

The wet-stripping formvar method of Schaefer and Harker³ is illustrated in Fig. 1*b*. Resolution is good with this method, but appears to be slightly inferior to that obtained with polystyrene-silica method. There are also areas lacking in detail, where perhaps the formvar did not wet the surface. The same is true of the

dry-stripping method used for Fig. 1c. The method illustrated in Fig. 1c, developed in this laboratory, consisted in stripping the formvar replica by means of intimate contact with scotch tape, then loosening the adhesive and freeing the formvar in a bath of xylol. Difficulties were encoun-

obtained thus far, however, is 40 Å., which is 100 times better than the optical microscope. Resolution in metallographic applications is limited by the details that can be developed by etching and transferred to a replica, and the present results indicate that two spots 150 Å. apart can be definitely

TABLE 1.—*Compositions and Treatments*

Metal	Analysis, Per Cent	Treatment
High-speed steel.....	C 0.70, Mn 0.24, Si 0.29, S 0.009, P 0.017, W 17.8, Cr 4.05, V 1.04, Ni 0.078	See Figs. 6 and 7 for heat-treatment
Copper.....	O.F.H.C.	Hot-rolled rod, annealed 1 hr. at 800°C.
Monel metal.....	Ni 66, Cu 29, Fe 1, Al 2.75	Fig. 11a—annealed at 1800°F. and water-quenched Fig. 11b—same as a plus 5 hr. at 1800°F. quenched in iced brine Fig. 11c—same as a plus 16 hr. at 1080°F. followed by furnace cooling at the rate of 14°F. per hour Fig. 11d—same as a plus 16 hr. at 1250°F. followed by furnace cooling at the rate of 13°F. per hour Fig. 10—same as Fig. 11a. Etched before deformation.
Tempered martensite.....	Ni 3.5, C 0.35, Cr 1.5	Austenitized 1650°F. for 2½ hr., quenched in water Figs. 4b and 4d—tempered 3 hr. in salt bath at 570°C. Fig. 5—tempered 3 hr. in salt bath at 527°C.
Spheroidized low-alloy steel..	Ni 3.5, C 0.35, Cr 1.5	Figs. 4a and 4c—tempered 3 hr. in salt bath at 275°C. Heated at 1650°F. for 2½ hr., quenched in water, tempered 3 hr. in salt bath at 480°C.
Spheroidized carbon steel....	0.60 C	Spheroidized 23 hr. at 775°C. Spheroidized 8 hr. at 650°C.

tered from fibrous material and dirt in the adhesive which are insoluble in xylol.

The specimens photographed in Figs. 1 to 13 are listed in Table 1 together with thermal treatments. All plates were exposed at magnifications of 2000 to 6300 and subsequently enlarged; the plates used were lantern-slide, contrast emulsion; the objective-lens pole piece was that originally supplied with the instrument.

DISCUSSION OF RESULTS

Resolution Obtained.—It will be recalled that the resolving power of a light microscope, which is limited by the wave length of the light used and the numerical aperture of the objective lens, seldom exceeds about 0.5 microns (5000 Ångstroms). The electron microscope, using a wave length only 1/100,000 that of ordinary light, and an electron lens having a numerical aperture of about 0.02 instead of the usual 1.2 to 1.4, should have a theoretical resolving power some 1500 times better. The best

resolved by the polystyrene-silica method, and roughly the same distances (perhaps slightly greater) by the formvar method.

Registration of Surface Contour.—Shadows and dark lines on the prints correspond to shadows in the electron pattern, and these occur where the replica appears thick and opaque to the electron beam. Now if a metal surface contains narrow grooves after etching, polystyrene will be pressed into the grooves and form projecting fins. It appears that silica is deposited uniformly over the surfaces of the flat places and on the sides of these polystyrene fins; all flat areas perpendicular to the electron beam then appear thin and transparent to the rays, while the fins, which present the film obliquely or edge-on to the beam, appear opaque. Projecting fins on the metal, which make narrow grooves in the polystyrene, register similarly. Abrupt steps at differences in level of the metal surface give dark lines. For example, if particles of one phase in a two-phase alloy



FIG. 4.—TEMPERED MARTENSITE. PICRAL ETCH.

- a.* Tempered to 400 Brinell hardness. $\times 5000$.
- b.* Tempered to 250 Brinell hardness. $\times 5000$.
- c.* Optical photomicrograph of 400 Brinell specimen. $\times 1500$.
- d.* Optical photomicrograph of 250 Brinell specimen. $\times 1500$.

stand in relief above the surface or are depressed below the surface they are surrounded by dark lines. Indirect evidence can frequently distinguish elevations from depressions.*

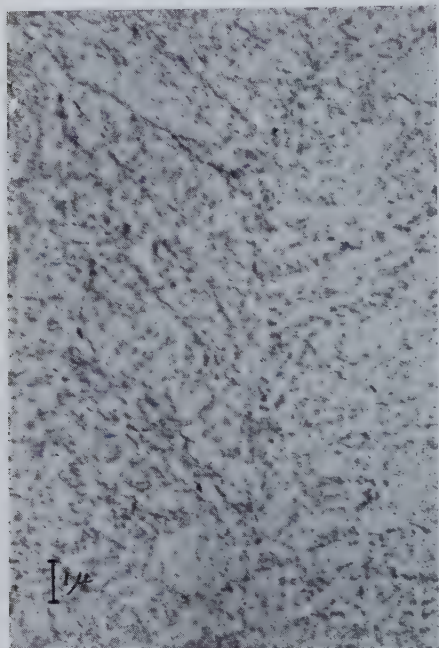


FIG. 5.—TEMPERED MARTENSITE IN LOW-ALLOY STEEL. 300 BRINELL HARDNESS. PICRAL ETCH. $\times 5000$.

Nature of Etch Attack.—The etched surfaces of single-phase metals and alloys frequently exhibit structures of remarkable interest, as will be seen from Figs. 8 to 12. It may be possible that the patterns produced are in some way related to galvanic effects in the etchant, but it seems more probable that the effects are due to variations in perfection of the crystalline grain,

since the patterns obviously change with grain orientation. The attack of the etching solution appears to be fastest along the boundaries of domains, much smaller than grains, which in copper are rod shaped (Fig. 8) and in Monel metal are equiaxed (Figs. 11b, 11d, 12d).† The rod-shaped domains seen on the surface of deeply etched copper show the following striking features:

1. The rod axes are approximately parallel in an individual grain, or at least in a large part of a grain, as if paralleling a crystallographic axis.
2. The rods are equiaxed in cross section, having diameters of 0.1 to 0.5 microns (1000 to 5000 Å.) and lengths up to at least 5 microns (50,000 Å.).
3. Different etching solutions have given patterns of similar character and roughly similar dimensions.
4. The patterns are always irregular and do not provide evidence of a regular periodic imperfection in the lattice that has sometimes been postulated.
5. The boundaries of the rods form a branching system of lines on the surface, resembling a map of rivers.

The domains in Monel metal are smaller than in copper and appear to be equiaxed blocks about 0.05 or 0.1 microns in size in the quenched material (Figs. 10, 11a, 11b) and about 0.2 microns in the overaged material (Fig. 11d, 12d). None were developed in the properly aged alloy (Fig. 11c), possibly because the etchant was controlled by the distribution of precipitate, a fact that suggests that perhaps the pattern in overaged Monel is controlled by the precipitate rather than by a pattern of imperfections.

† An alternative interpretation is that the boundaries of these domains are attacked more slowly than the interiors and stand in relief. Although the pictures do not differentiate between these alternatives directly, the nature of the etch attack of a grain in polycrystalline copper at a grain boundary strongly suggests that the dark lines represent grooves in the metal, and thus that the boundaries are attacked more rapidly (see Fig. 8a).

* The problem of deducing specimen contour from the photographs is treated in a current paper by R. D. Heidenreich.⁴ Stereoscopic pictures are recommended. However, even with these, in order to distinguish hollows from bumps and projecting fins from grooves, it is necessary for the operator to know which side is which on the silica replica; for example, by comparing the electron stereoscopic pictures with optical examination of the same spot on the specimen.

If we assume, tentatively, that these domains are the mosaic imperfections in crystals about which so much has been written, it seems reasonable that each block, being approximately a perfect crystallite tilted slightly from its neighbors, should be attacked more slowly than the transition layers at the boundaries of the blocks. Furthermore, the blocks are of the order of size that has been deduced from other evidence (Table 2).

TABLE 2.—Order of Size of Blocks

Dimensions, Microns	Nature of Evidence	Reference
0.01 to 1..	X-ray reflecting power	Darwin ⁵
0.8.....	Stratification in Zn and Cd	Straumanis ⁶
0.54.....	Segregation of Po in Bi	Focke ⁷
1-2.....	Dislocation paths (theoretical)	Taylor, Koeler ⁸
0.5 dia. by 1 to 5 long....	Electron microscope, Cu	Present paper
0.2 to 0.5.	Electron microscope, K-Monel	Present paper

Cold-work appears to have the effect of fragmenting the domains in copper, producing more small ones, as will be seen from Figs. 9c and 9d, and making the etching attack much less uniform. In some instances banded effects are produced (Fig. 9d). Dimensions of 0.1 to 0.15 microns are common, which is about the size (0.07 microns) estimated by Wood⁹ for fragments in cold-worked copper, as judged by the uncertain method of widths of X-ray diffraction lines. This is also the lower limit (0.1 microns) assigned to fragment size in cold-worked (filed) copper by Brindley and Ridley¹⁰ on the basis of X-ray line widths and intensities.

Spacings of Slip Lines.—A large number of slip lines have been photographed in polycrystalline samples of copper and Monel metal, a few of which are reproduced in Figs. 9a, 9b and 10. The spacings of slip lines are greater—at these amounts of deformation—than the dimensions of the blocks revealed by etching. Distribu-

tion curves for the spacings of the slip lines that were measured are given in Fig. 14. It is interesting to note that there is a marked tendency for the lines in Monel to be spaced 0.3 microns apart after a compression of a few per cent, while in copper that had received a similar amount of deformation by compression there was no preferred spacing between 0.3 and 2.5 microns. The number of measurements made is too few to permit, at best, more than semiquantitative conclusions from the distribution curves.

Spacings of Pearlite Lamellae.—In the photomicrographs of the finest pearlite that could be produced in eutectoid plain carbon steel by a gradient quench (Figs. 1a and 1b) it was found that the minimum interlamellar spacing that occurs with reasonable frequency is about 0.05 microns (500 Å.); a mean value is 0.11 microns (1100 Å.). The nonlamellar areas in Fig. 1a have dimensions approximately the same. These dimensions compare well with the spacings deduced less directly from optical photomicrographs (800 Å. for pearlite formed isothermally at 600°C. in eutectoid plain carbon steel)¹⁴ and with the minimum spacings found by Mehl¹⁵ with the silver-collodion replica method.

Spacings of Precipitated Particles.—The precipitate causing age-hardening in K-Monel metal is in an extremely fine state of dispersion, and Fig. 11c contains the smallest details of any of the pictures taken in this laboratory up to this time. Many of the particles are spaced no more than 0.03 micron (300 Å.) apart, and 0.05 micron spacings are common. There is a suggestion of platelike shapes of the precipitate, and of a Widmanstätten pattern in the alloy when aged to maximum hardness, as in this figure.

Comparisons with Theories of Strength of Metals.—Orowan¹¹ has suggested that the critical resolved shear strength for slip, τ , is related to the spacings of slip

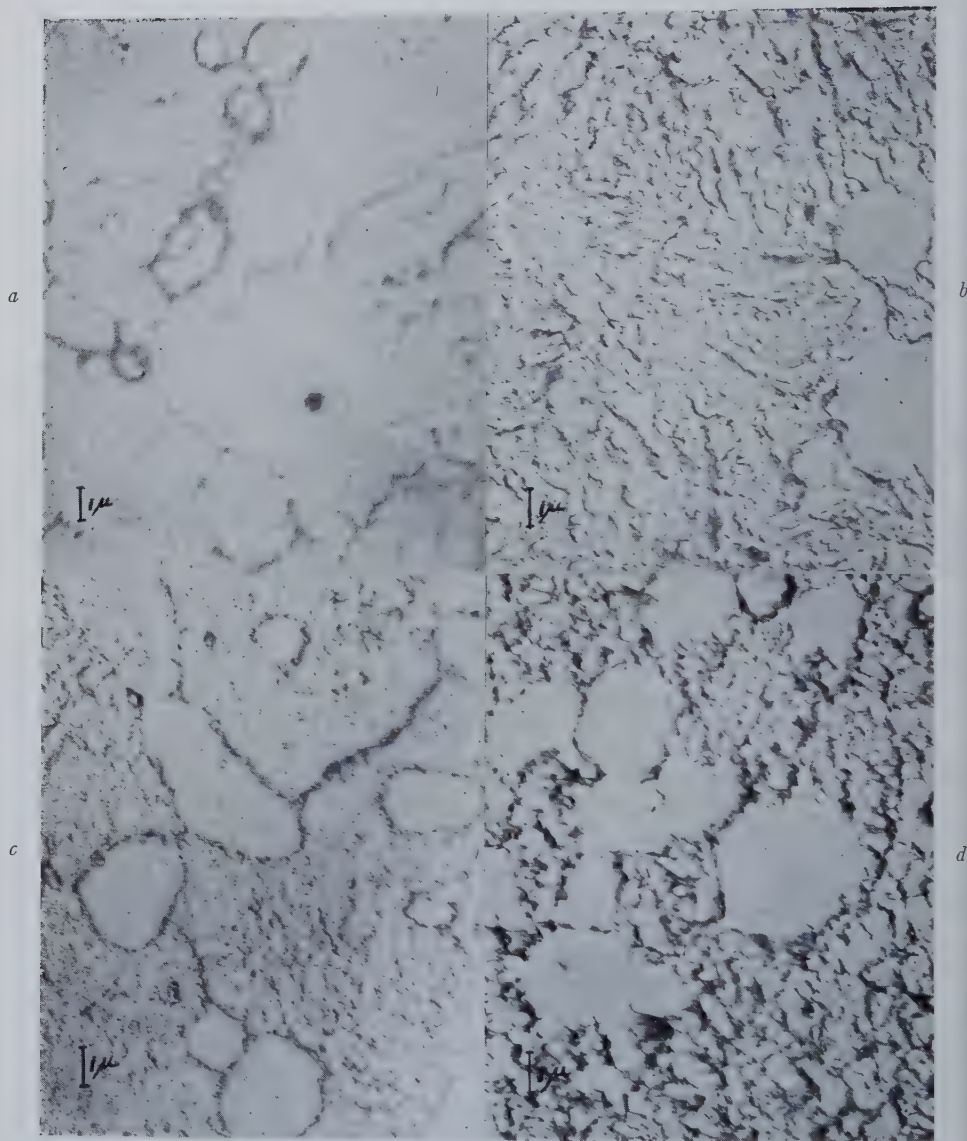


FIG. 6.—HIGH-SPEED STEEL. FIRST PREHEATED 20 MINUTES AT 1550°F., THEN 2 MINUTES 45 SECONDS AT 2350°F., OIL-QUENCHED. $\times 5000$.

- a. No tempering. Rockwell C. 65.6. Etched 8 minutes in 4 per cent nital.
- b. Undertempered. Tempered 1 hour at 510°F. Rockwell C. 60.8. Etched $7\frac{1}{2}$ minutes in 2 per cent nital.
- c. Properly tempered. Tempered 1 hour at 1020°F. Rockwell C. 64.5. Etched $7\frac{1}{2}$ minutes in 2 per cent nital.
- d. Overtempered. Tempered 1 hour at 1290°F. Rockwell C. 46.2. Etched $1\frac{1}{2}$ minutes in 2 per cent nital.

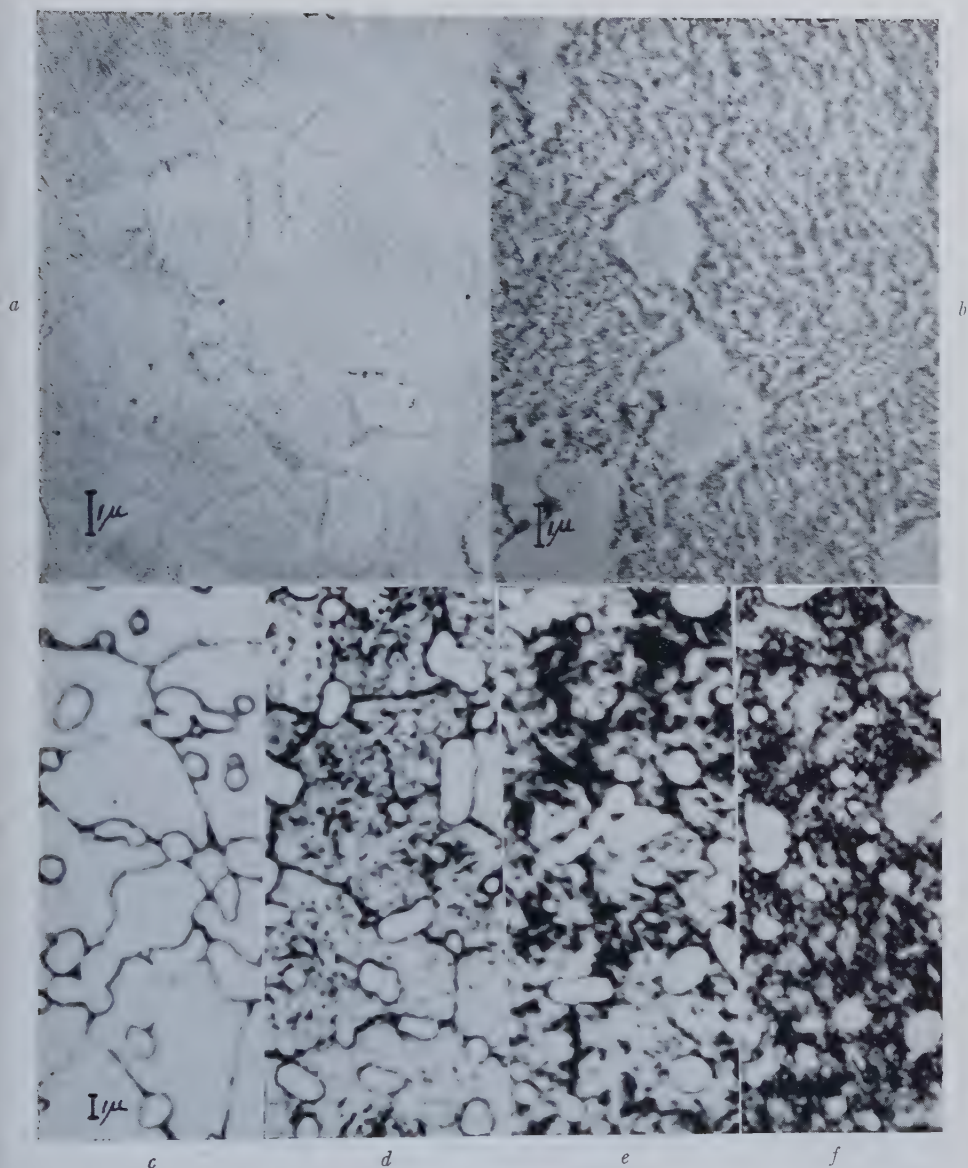


FIG. 7.—HIGH-SPEED STEEL.

- a.* No tempering. Etched 5 minutes in $\frac{1}{4}$ per cent nital. $\times 5000$.
b. Overtempered. Etched 1 minute in $\frac{1}{4}$ per cent nital. $\times 5000$.
c. Optical photomicrograph, same surface used for Fig. 6*a*. $\times 2500$.
d. Optical photomicrograph, same surface used for Fig. 6*b*. $\times 2500$.
e. Optical photomicrograph, same surface used for Fig. 6*c*. $\times 2500$.
f. Optical photomicrograph, same surface used for Fig. 6*d*. $\times 2500$.

planes in severely deformed metals by the formula

$$\tau = \frac{GS}{2\pi h} \quad [1]$$

where G is the shear modulus, S is the atomic spacing in the direction of slip and h is the spacing between active slip planes. From the curve for quenched Monel metal in Fig. 14, h may be taken as 3000 Å. and, if $G = 9,500,000$ and $S = 2.5$ Å., the strength calculates to 1300 lb. per sq. in. (resolved shear stress). The yield strength for an alloy in this condition is 50,000 lb. per sq. in., which would correspond to a maximum resolved shear stress of 25,000 lb. per sq. in., hence the theoretical value is greatly in error. No particular value can be chosen for copper. Spacings around 2000 and 3000 Å., with $G = 6.48 \times 10^6$ and $S = 2.56$, correspond to stresses of 130 and 90 lb. per sq. in., respectively, and still greater spacings must occur frequently. Eq. 1 therefore predicts a very low yield strength for copper, a stress-strain curve that begins to round off at low stresses, and this is, of course, a familiar characteristic of copper. There appears to be a qualitative but not a quantitative agreement between these very fragmentary experiments and the theory mentioned above.

Bragg¹² has developed this thought somewhat further by applying the principle that when slip occurs the strain energy after slip must be less than the strain energy before slip. Bragg assumes that the elastic shear-strain energy of each mosaic block of the metal is reduced by a slip movement within the block, slip consisting of a movement by one atomic distance in the direction of slip, the distance S . If the thickness of the block is t , the strain energy in a cubic block before slip is $\frac{1}{2}GV(x/t)^2$ where V is the volume of the block and x/t is the elastic shear. After slip this is altered to $\frac{1}{2}GV[(x - S)/t]^2$, which must be a smaller value than the first if

slip is to occur. Hence x must be greater than $S/2$. Since the maximum applied shear stress is not, in general, parallel to the slip plane, x must be about equal to S and therefore the resistance to shear should be given by the approximate relation

$$\tau = G \left(\frac{S}{t} \right) \quad [2]$$

and the resistance to tensile stress should be 2τ . Bragg applied this equation to the mosaic fragments that have been estimated in various cold-worked metals from X-ray line widths, with considerable success: theoretical tensile strength in copper, 48,000 lb. per sq. in.; in "pure iron," 18,000 lb. per sq. in.; in "pure aluminum," 2000 lb. per sq. in. If one assumes that the domains brought out by etching and the spacings between particles in the photomicrographs of this paper are the blocks that act as units in the way postulated by Bragg, the tensile and yield strengths computed from Eq. 2 are as given in Table 3.

TABLE 3.—*Theoretical Strengths Estimated from Block Size by Equation 2*

Metal	Block Size t , Å. (Approximate)	Theoretical Yield Strength, Lb. per Sq. In.	Strengths Observed
Copper, annealed	3,000 ^a	11,000	
Copper, compressed 75 per cent.....	1,000	33,000	34,000 (tensile)
K-Monel, quenched.....	1,000	47,000	50,000 (yield)
K-Monel, aged.....	500	95,000	120,000 (yield)
K-Monel, overaged.....	2,000	34,000	100,000 (yield)
Pearlite (finest).....	500	115,000	170,000 (yield) ^b
Pearlite, mean interlamellar spacing.....	1,100	52,000	

^a Diameter of rod-shaped domains.

^b Extrapolated value from isothermal reaction experiments.¹³

Structure of Tempered Martensite.—It has been very difficult to get reproducible and trustworthy results with tempered martensite (see, for example, Fig. 13). By comparing the appearance of spheroid-



FIG. 8.—HIGH-PURITY COPPER, ANNEALED 1 HOUR AT 800°C. $\times 10,000$.
a, b and c. Potassium dichromate, sodium chloride, sulphuric acid etch.
d. Ferric chloride, hydrochloric acid etch.

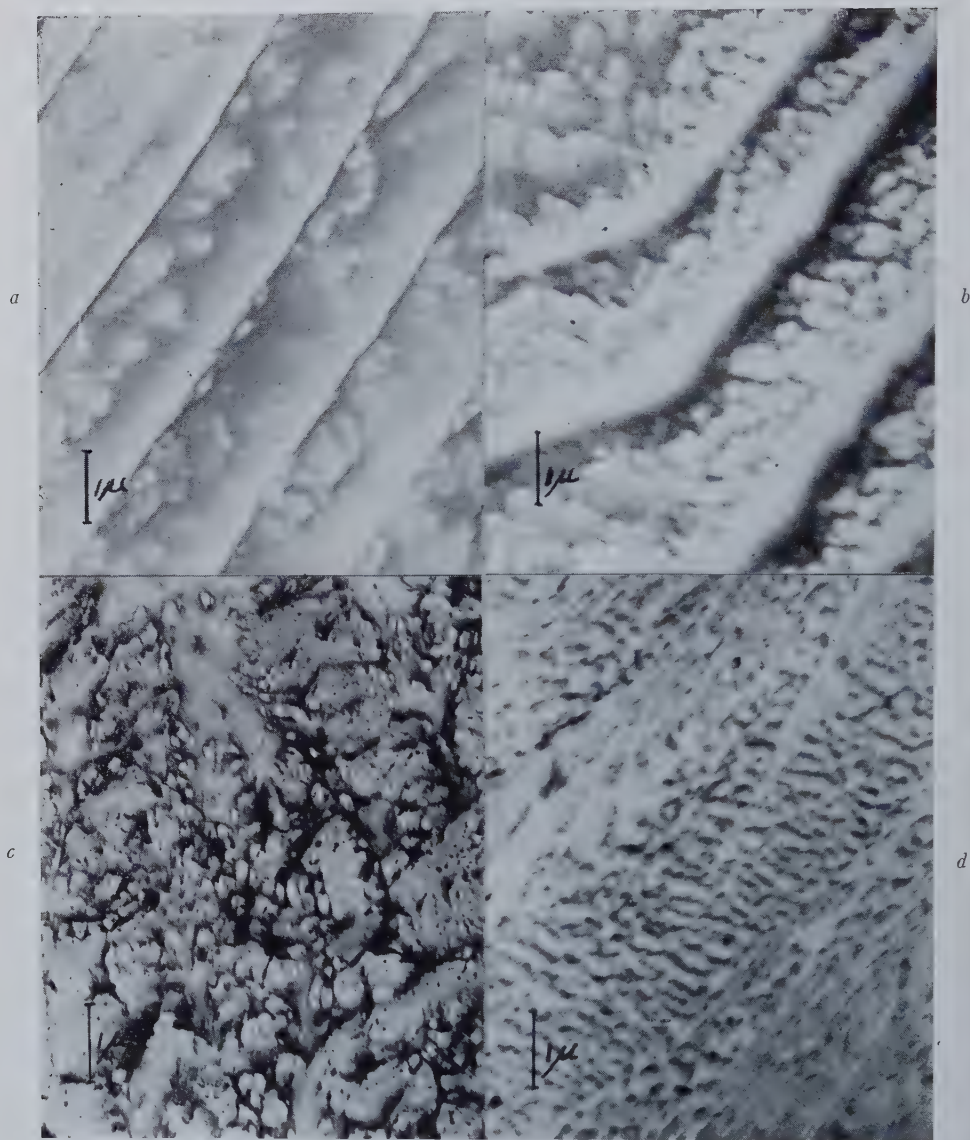


FIG. 9.—HIGH-PURITY COPPER. DICHROMATE ETCH. $\times 10,000$.
a and *b*. Slip lines produced by 5 per cent compression. Etched before compression.
c and *d*. Compressed 72.1 per cent. Polished surface perpendicular to plane of compression. Etched before compression.

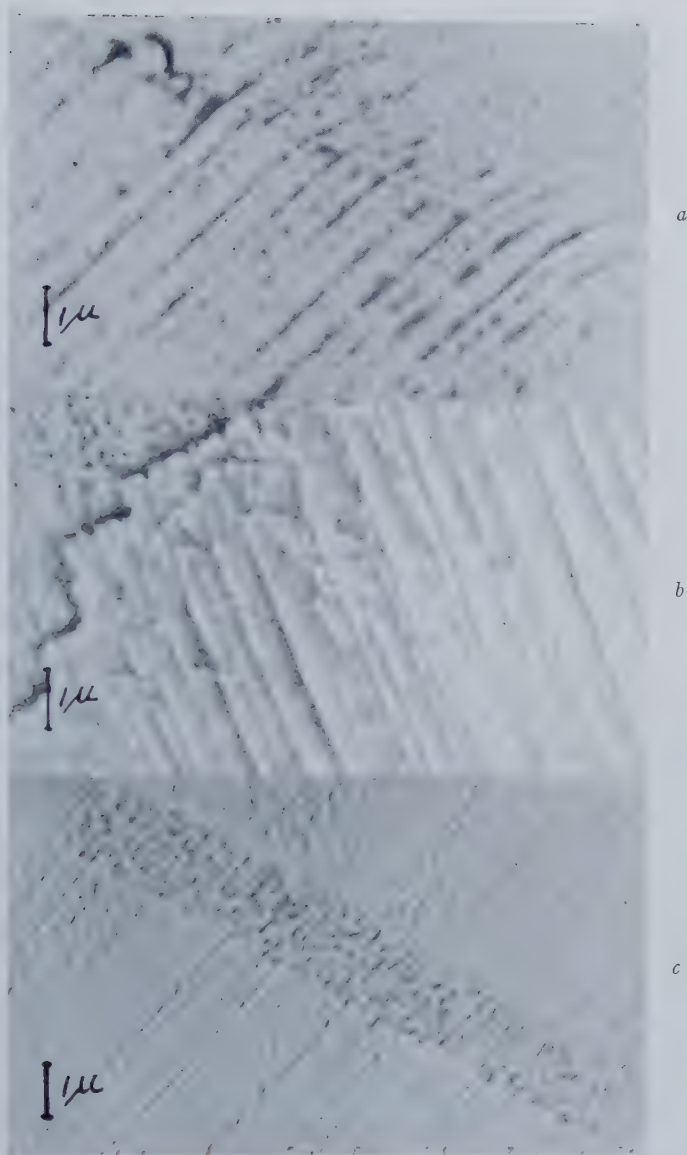


FIG. 10.—SLIP LINES IN K-MONEL, AS QUENCHED. ELECTROLYTIC ETCH FOLLOWED BY COMPRESSION.
a. 5 per cent deformation. $\times 8000$.
b. 5 per cent deformation. $\times 8000$.
c. 10 per cent deformation. $\times 7200$. Shows annealing twin.

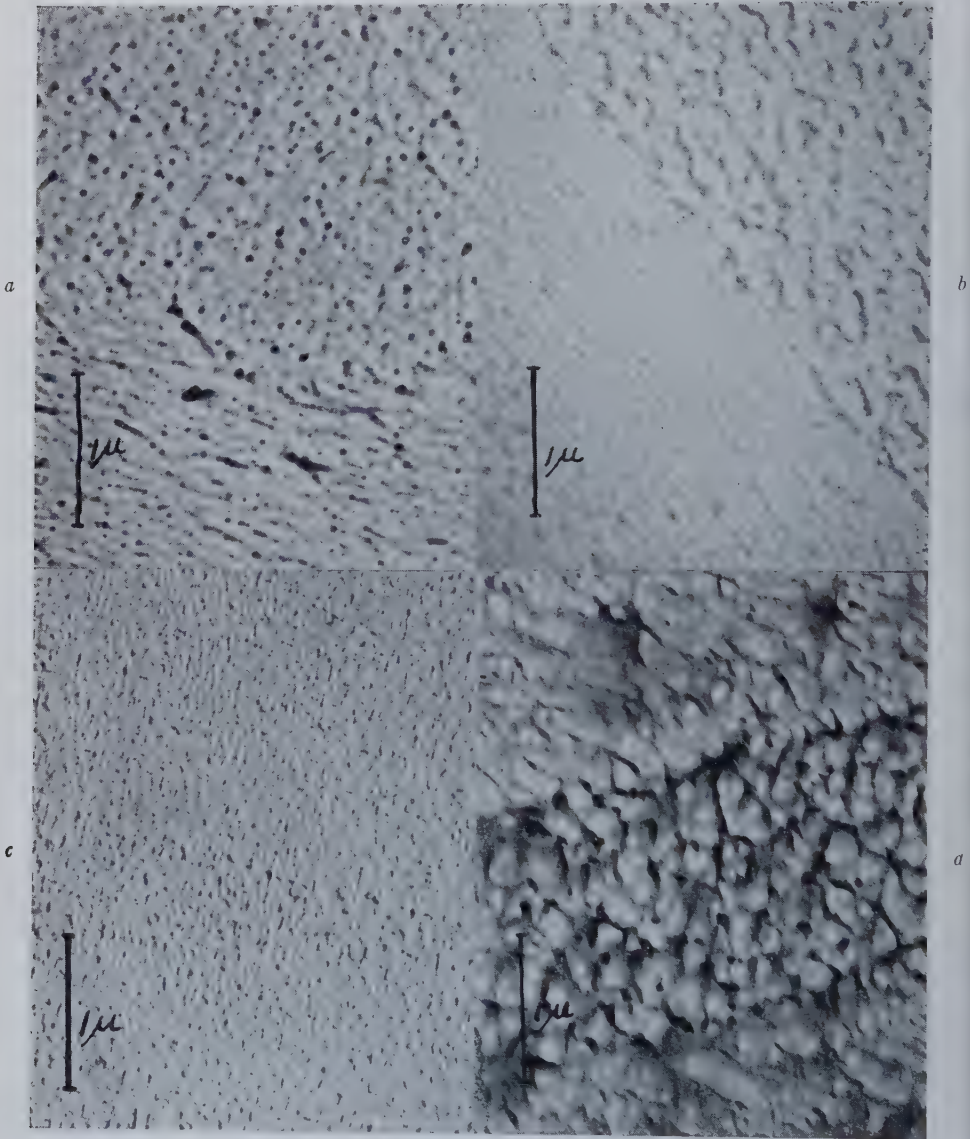


FIG. 11.—K-MONEL METAL WITH VARIOUS HEAT-TREATMENTS. $\times 20,000$. ELECTROLYTIC ETCH.
(10 PER CENT HNO_3 , 5 PER CENT CH_3COOH .)

- a.* As quenched in water, 161 Brinell hardness.
- b.* As quenched in iced brine.
- c.* Aged to maximum hardness, 301 Brinell hardness.
- d.* Overaged, 255 Brinell hardness.

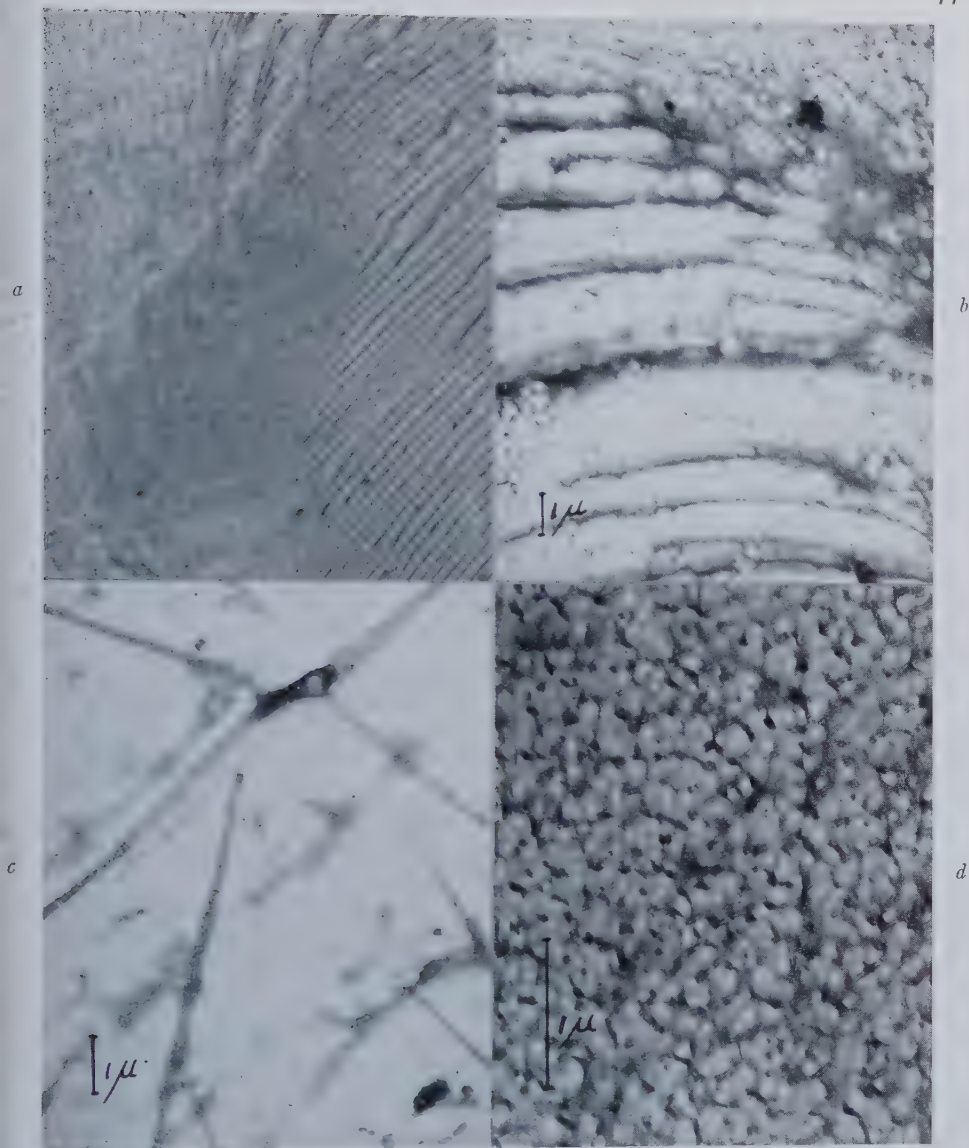


FIG. 12.—TYPICAL FALSITIES, "ARTIFACTS."

a. Optical photomicrograph of defective polystyrene replica from tempered martensite. Shows styrene lines. $\times 200$.

b. Electron photomicrograph of *a*. $\times 5000$.

c. Electron photomicrograph showing folds in silica film. $\times 8000$.

d. Electron photomicrograph showing image doubling. (Specimen of Fig. 11*d*, K-Monel.) $\times 20,000$.

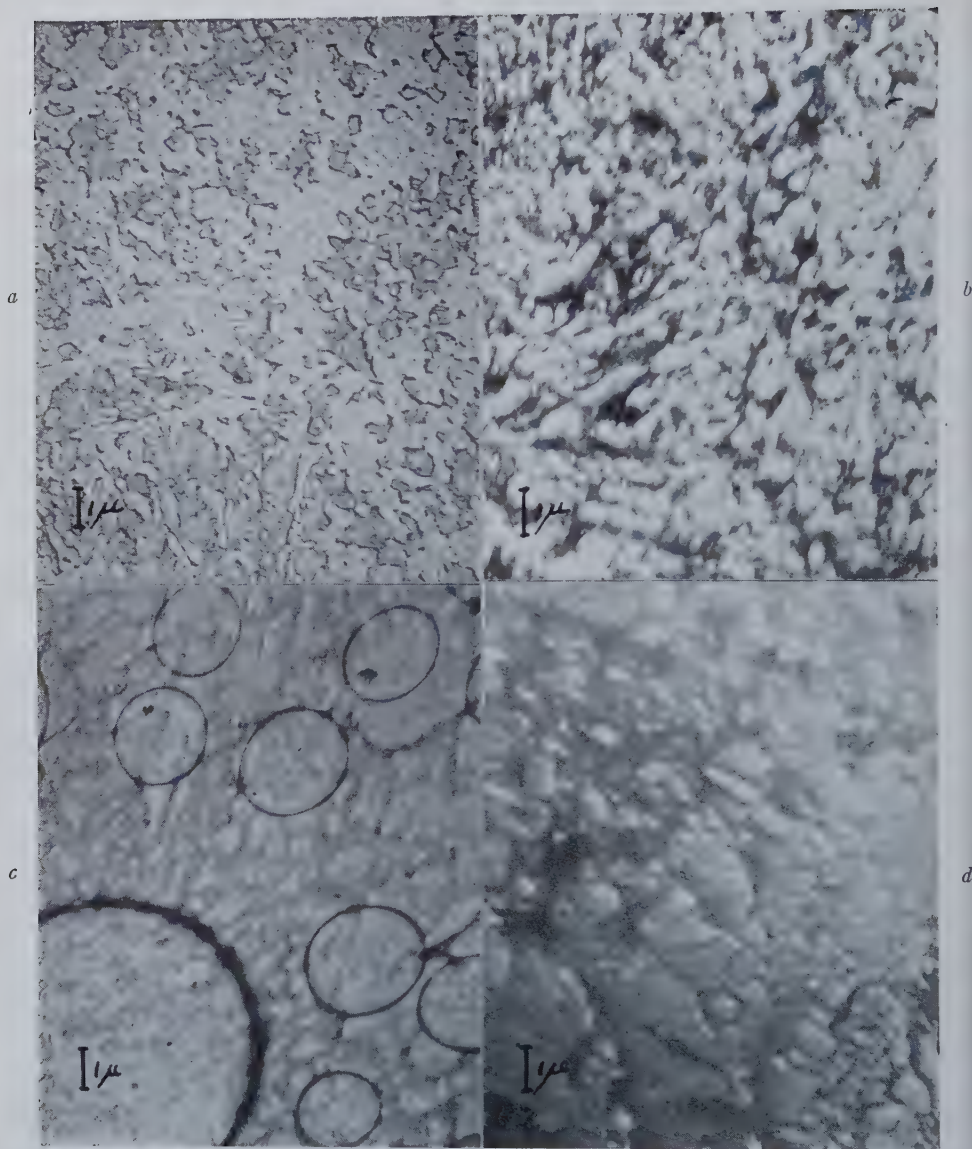


FIG. 13.—TYPICAL FALSITIES, "ARTIFACTS."

a. Tempered martensite, 350 Brinell. Appearance probably due to disturbed metal not completely removed by etching. Very light picral etch. $\times 5000$.

b. Tempered martensite stained during polystyrene molding. 400 Brinell specimen. Very light nital etch. $\times 6000$.

c. Silica film of tempered martensite which has not been washed properly in ethyl bromide. Rings are from polystyrene. 400 Brinell specimen. $\times 5000$.

d. Silica film from faulty polystyrene replica of tempered martensite. $\times 6000$.

ized steels, Fig. 3, with quenched and tempered steels polished and etched in the same manner, some measure of confidence was attained, but the differences between

fresh metal, unroughened by etching and free from evidence of mosaic structure, which appear white on the print. The width of these strips corresponds to a displace-

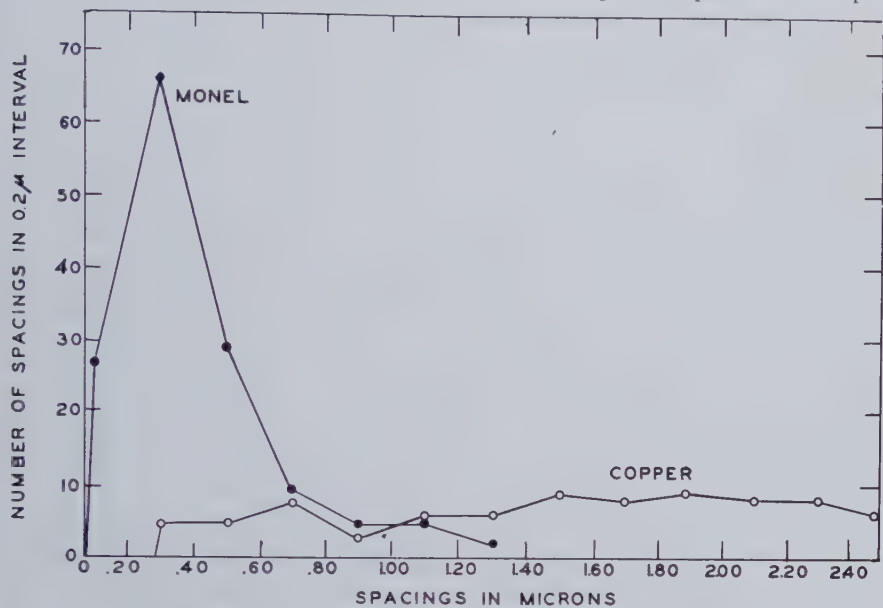


FIG. 14.—DISTRIBUTION OF SLIP-LINE SPACINGS AFTER COMPRESSION OF 5 TO 10 PER CENT.

the structures of Figs. 4a, 5b and 5 are still greater than they should be and doubtless indicate some variations in polishing or etching effects. Electrolytic polishing is being resorted to but this also gives the various structures of Figs. 4, 5, 13b and 13c.

Structure of Slip Lines.—It is evident from Figs. 10 and 11 that slip planes intersecting the surface nearly perpendicularly produce a stepped surface with sharp step edges. Deformation at each plane appears to be confined to a plane or to a zone less than 200 or 300 Å. wide. (How much less than this one cannot say because the thickness of the silica replica and the rounding of its upper surface at the edge of the step limit the resolution.) There is no evidence of closely grouped slip lines at each major step. The appearance of Fig. 9b is accounted for if slip planes come to the surface obliquely and expose strips of

ment of about 0.5 microns. If these white strips, owing to an optical illusion, appear to the reader to stand up from the etched surface, they may be made to appear as furrows in the surface by merely turning the page upside down.

ACKNOWLEDGMENTS

The work reported here was made possible by funds granted by the Bristol-Myers Co. for the purchase of the instrument. All electron microscope photographs in this paper were taken by Mary South Fravega; with the exception of the specimens of Figs. 1 and 6, all specimens were prepared for metallographic examination by Elizabeth A. Saffer or by Mrs. Fravega; the enlargements were made by Miss. Saffer. We are indebted to Messrs. N. B. Pilling and J. T. Eash, of the International Nickel Co., for the samples of Monel metal, to Mr. George Roberts, of the Vanadium

Alloys Steel Co., for the specimens of high-speed steel, and to Messrs. R. A. Colton and Arthur Westerman for the steel specimens of Figs. 1, 3, and 4.

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DISCUSSION

(E. E. Schumacher presiding)

E. R. PARKER,* Schenectady, N. Y.—I have just one addition to make which may be useful to those who are interested in using the formvar replica for obtaining electron micrographs. In the General Electric Research Laboratories, a Scotch-tape removal process has been used for stripping formvar from the samples, and in the technique used it has been possible to avoid the contamination of the formvar replica by the Scotch tape by cutting a $\frac{1}{8}$ -in. diameter hole in the Scotch tape over

the section of the replica that is to be viewed under the microscope. When the Scotch tape is pulled from the sample, the part under the hole comes off with the remainder of the stripping. Then it can be cut from the Scotch tape. This makes it unnecessary to use a solvent to remove it from the tape. In that way it is possible to avoid the contamination introduced by the Scotch tape.

F. KELLER,* New Kensington, Pa.—Dr. Barrett has indeed given a very interesting and timely paper on the use of the electron microscope for metallographic work. There is little doubt in the minds of those who have used the microscope that it will be helpful in the study of structures that are now sub-microscopic. The electron microscope has very high resolving power but at present the limitations are the methods of preparing samples to utilize the high resolving power. Dr. Barrett mentioned two of the methods that are used; namely, the formvar replica and the evaporated silica replica. Both of these depend on differences in thickness to give the image.

There is a third method that has not been used to any extent in this country, which gives excellent results on some alloys at least. It is the oxide-film method. For aluminum alloys, it has been possible to produce an oxide film of satisfactory thickness, which does not show any structure and in which the constituents of the alloy remain in place. These constituents being of different atomic weights than the matrix will have different absorption characteristics. Thus, it is possible to have a positive electron microscope specimen instead of a replica.

I think that when more satisfactory methods of sampling are worked out, we will be able to get a great deal of information in a range of alloy structures that have been submicroscopic but on which a lot of speculation has been done as to what is actually present.

A. H. GEISLER,* New Kensington, Pa.—Dr. Barrett has found that the domains developed within the grains by deep etching are rod-shaped in copper and are equiaxed in Monel metal. The patterns are not regular and

* General Electric Company.

* Aluminum Research Laboratories.

show very little resemblance to the cubic structure of these metals. However, work done with deep-etched aluminum shows that the domains appear as well-developed cubes and apparently are related to the crystalline structure of the aluminum. This relationship is evident in the electron micrograph of a deep-etched aluminum alloy shown in Fig. 1. The micrograph shows the cubic structure in two differently oriented grains adjacent to a grain boundary. The electron microscope specimen in this case was a special oxide film stripped from the deep-etched sample.

L. S. BIRKS,* Washington, D. C.—Have you taken any pictures on unetched pearlite, Dr. Barrett?

C. S. BARRETT.—No, we have not.

L. S. BIRKS.—A method of electrolytic polishing has been developed which will not etch the surface of pearlite or tempered samples. A replica made after polishing shows a mosaic background but none of the pearlite lamellae appear and in tempered samples no coalesced carbides or other structure.

A very light etch at low temperature on the same surface then brings out structures comparable to those seen on a light microscope.

R. C. WOODWARD,† South Milwaukee, Wis.—This question, Dr. Barrett, is very elementary. On your Fig. 2*b*, of pearlite in eutectoid steel, there appears to be a tendency to pull the metal from the top of the illustration to the bottom; is that due to cold working and polishing?

C. S. BARRETT.—No, I think there is no smearing shown in Fig. 2*b*. I think the fractured edges of the carbide lamella stick up at an angle to the surface instead of perpendicular to the surface, as they do in Fig. 2*a*.

R. W. PARCEL,* Denver, Colo.—I should like to ask some of these men who have worked with the electron microscope if they have at this stage found it of any particular disadvantage in loss of colors in various alloys, which the optical microscope often discloses?

C. S. BARRETT (author's reply).—Mr. Parker's comments on the dry stripping of formvar replicas are a welcome addition to the paper. We have tried some of the techniques developed by Schaeffer and Harker at the G. E. Research Laboratories for stripping formvar replicas and have sometimes had success with them. On the whole, however, we find it a disadvantage to be required to have such a light etch that the formvar can be easily removed. With many of the etched surfaces we have tried to examine, we have been able to strip the formvar from the surface only where the Scotch tape actually touched the film. The polystyrene-silica method, on the other hand, can be applied either to a lightly etched or a deeply etched surface.

I think many excellent electron micrographs may be expected from the oxide-film method in the hands of Mr. Keller and Dr. Geisler.

Mr. Parcel's question of the disadvantage resulting from the loss of color in electron micrographs is, of course, pertinent. Much of the metallographer's lore has to do with color; however, color is still available in the range of magnification of the optical microscope and most constituents of alloys are visible in this range or can be made so with appropriate heat-treatment. The electron microscope can hardly be expected to supplant the optical, but merely supplement it in certain problems where its extreme resolution justifies the added labor and time required, hence the lack of color in images is not very serious in metallography. In the study of bacteria and viruses the lack of ability to employ stains may be a relatively greater disadvantage.

* Naval Research Laboratory.

† Bucyrus Erie Company.

* Denver and Rio Grande Railroad Laboratories.

Application of Electron Microscope to Study of Aluminum Alloys

By F. KELLER* AND A. H. GEISLER,* JUNIOR MEMBER A.I.M.E.

(New York Meeting, February 1944)

SOME of the important changes that take place in the structure of aluminum alloys are largely submicroscopic in character. This is especially true of the changes that accompany age-hardening and recrystallization. Although improved metallographic practices have been helpful in indicating some of these changes indirectly, results are limited by the resolving power of optical microscope lenses. The electron microscope, however, provides a new and important means for investigating the fine structure of metals in a range not possible heretofore. It is anticipated that this microscope will yield new and useful information to metallurgists when suitable techniques are developed to utilize its very high resolving power.

Several unique methods have been devised to permit the examination of the structure of opaque samples by the electron microscope. These are all based on the principle of producing a very thin film that represents the prepared surface of the opaque metal sample, which can be examined in the transmission microscope; however, the available methods fall into three categories, depending on the manner in which the film is obtained.

With the oxide-film method developed by Mahl³⁻¹⁷ a very thin surface layer of the metallographic sample is converted

into oxide by a thermal, chemical or anodic treatment. After removal from the metal sample by one of the special techniques described by Evans,¹⁹ this oxide film is examined in the electron microscope, and is found to portray the structure of the original metal surface. Films formed on aluminum,^{8,17} nickel,⁷ iron^{3,8,9} and a nickel-beryllium alloy¹¹ by heating; films formed on iron^{8,9} by chemical action; and films formed on aluminum³⁻¹⁶ by anodic oxidation, have been examined.

The other two are more recent methods developed principally in this country; they consist in making the thin film in the form of a mold or replica of the surface contour of an etched sample. With the negative replica method the thin film is made directly on the sample; with the positive replica method it is made on a negative reproduction of the sample. With both methods, variations in the contour of the metal sample, caused mainly by etching, produce variations in the thickness of the surface replica. Because of the direct dependence of the amount of scattering of the illuminating electrons upon the thickness of the film penetrated, only the variations in thickness of the replica are responsible for tones in the electron image.

Negative replicas are made by forming a thin film of some suitable material directly on the polished and etched metal sample, and derive their name from the fact that after removal from the sample they have the high and low points in the sample reversed, as shown in Fig. 1. Nega-

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* Metallography Division, Aluminum Research Laboratories, Aluminum Company of America, New Kensington, Pennsylvania.

³ References are at the end of the paper.

tive replicas for the examination of metallographic samples have been made by flowing onto the metal surface solutions of lacquers such as collodion^{4,11,12,20} or form-

process in which an initial negative mold is first made from the metal surface and then the thin replica is made from the initial mold. Positive replicas are so named

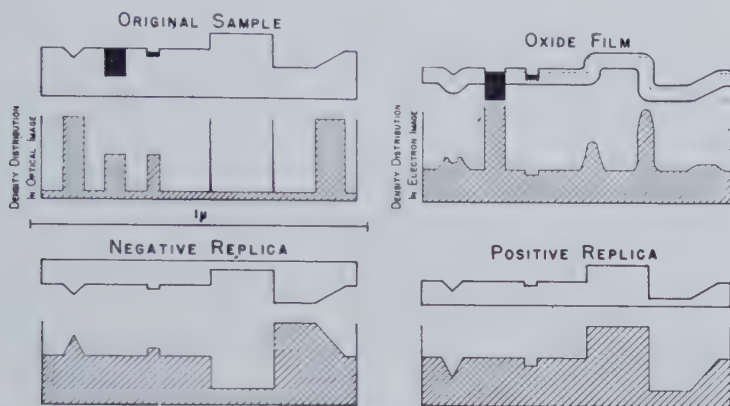


FIG. 1.—SCHEMATIC REPRESENTATION OF SPECIMENS MADE BY DIFFERENT METHODS, AND DENSITY DISTRIBUTION OBTAINED WITH THESE SPECIMENS.

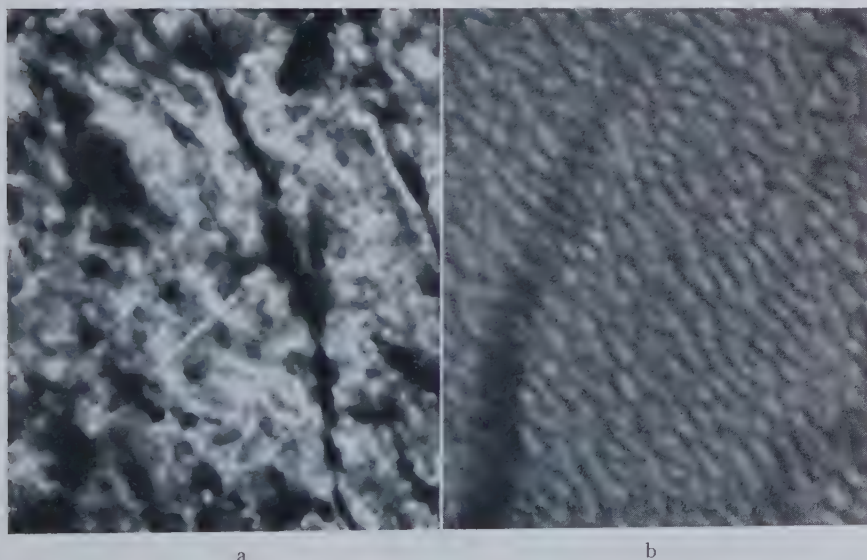


FIG. 2.—OXIDE FILMS THAT SHOW A DEFINITE STRUCTURE FOR THE OXIDE.

a. Film formed by heating a 0.9 per cent silicon alloy. $\times 20,000$.

b. Film formed on 99.95 per cent aluminum by anodic oxidation in a chromic acid electrolyte. $\times 110,000$.

var^{1,2,21-23} in volatile solvents and by evaporating or electrodepositing metals such as aluminum,²⁰ beryllium²⁴ or chromium¹² onto the sample surface.

Positive replicas are made by a two-step

because they have high and low points corresponding directly to those of the metallographic sample as shown in Fig. 1. The silver-collodion positive replica method^{1,25,26} consists of electrodepositing

a relatively thick layer of silver onto the polished and etched sample, removing the sample from the silver, flowing a

The polystyrene-silica method,^{1,2,27,28} consists of making the initial impression by molding the sample in polystyrene. After



FIG. 3.—APPEARANCE OF CONSTITUENT PARTICLES OCCLUDED IN ANODIC OXIDE COATINGS

a. Cross section of an anodically coated 20 per cent silicon alloy showing particles of silicon in the oxide coating. $\times 500$.

b. Oxide film from a 3 per cent manganese alloy showing the constituent particles as they appear with vertical, reflected light. $\times 500$.

c. Same as *b* but with transmitted light. $\times 500$.

solution of collodion onto the silver and removing the thin collodion replica from the silver after the solvent has evaporated.

the metal is removed, a very thin film of silica is evaporated upon the initial polystyrene mold. The silica replica is then

removed by dissolving the polystyrene with ethyl bromide.

The choice of the particular process to be used depends to a large extent upon the

or condition of the metal specimen. In general, oxide films formed on samples by heating are not satisfactory because they are very porous and do not portray the

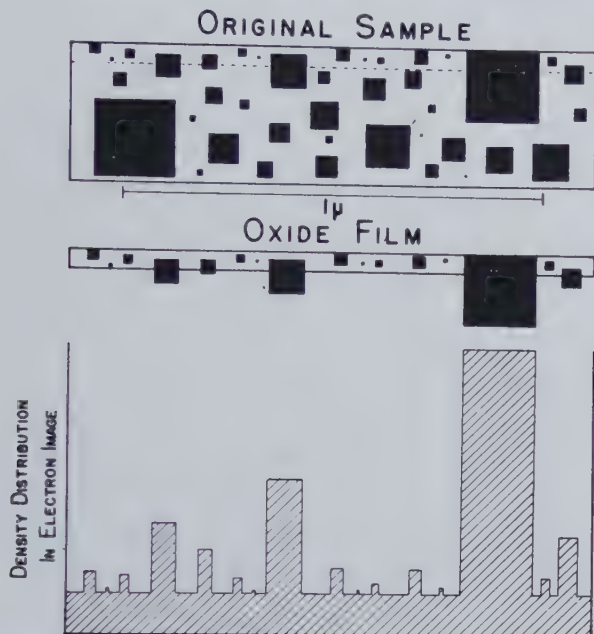


FIG. 4.—SCHEMATIC DIAGRAM SHOWING EFFECT OF CONSTITUENT PARTICLES IN OXIDE FILM ON DENSITY DISTRIBUTION IN ELECTRON MICROSCOPE IMAGE.

metal or alloy to be examined and upon the specific features under investigation. Although the oxide-film method is found generally useful for the study of aluminum, satisfactory oxidation techniques are not yet known for all metals. This paper presents some of the results that have been obtained with both the oxide-film method and some of the replica methods in the study of aluminum alloys with the electron microscope.

STRUCTURELESS OXIDE FILM FROM ALUMINUM

Oxide films for use in studies of metallographic structures with the electron microscope should not display interfering features that are dependent primarily upon the manner in which the oxide film is formed and independent of the nature

metal structure adequately. This is demonstrated by Fig. 2*a*, which shows an electron micrograph of an oxide film formed on an aluminum-silicon alloy sample by heating.

Oxide films formed by anodic oxidation of aluminum in the electrolytes normally employed to produce protective coatings show a granular structure characteristic of the oxide when the films exceed a specific thickness less than the thickness most suitable for samples for the electron microscope. When films made in these electrolytes are formed to the required thickness, a granular structure of the oxide is always present, which tends to obscure the structure of the metal specimen. This is demonstrated by Fig. 2*b*, which shows an oxide film formed on aluminum by anodic oxidation in a chromic acid elec-

trolyte. Similar granular structures are observed for films formed in sulphuric acid, oxalic acid and borax-boric acid electrolytes.³⁰

Two anodic oxidation treatments that produce almost structureless oxide films have been used by Mahl and others to study the microstructure of aluminum and its alloys. One treatment that employs an aqueous solution of borax and boric acid as the electrolyte³⁻¹⁵ has been used more extensively than the other. Thin films formed in this electrolyte, probably corresponding to the barrier layer, appear structureless;⁸ however, thicker films exhibit at magnifications of about 10,000 or greater a structure somewhat similar to that shown in Fig. 2*b*. The second previously used anodic oxidation treatment involves use of an aqueous solution of ammonium borate as the electrolyte.^{7,16} The films formed by this process generally have a granular texture¹⁶ but thin films can be formed that show little apparent structure (Fig. 10).

The preliminary object of the present research was to develop an oxidation technique for making films for portraying the microstructure of aluminum and alloys without a superimposed characteristic oxide structure. Although fair results were obtained from films made in borax-boric acid and ammonium borate electrolytes, an improved technique was desired. That a highly satisfactory technique was found is demonstrated by the electron micrographs included in this paper.

The new procedure is also an anodic treatment, and consists of making the metallographic specimen the anode in an electrolyte containing 12 per cent disodium acid phosphate (Na_2HPO_4) and 0.4 per cent sulphuric acid in water, and using a lead cathode. The film thickness is dependent principally upon the applied potential and not upon the length of treatment in contrast to films formed in some of the other electrolytes that

continue to grow rapidly in thickness with time. Potentials of 20 to 40 volts yield films of satisfactory thickness for electron microscope specimens. No difference in thickness could be detected in films formed by oxidizing for $\frac{1}{2}$ to 45 min., consequently a time of 3 to 5 min. was selected, merely for convenience.

Removal of the film is accomplished easily by using the mercury method.^{18,19} The oxide film on the surface being investigated is cut into small squares by scribing a network of lines about $\frac{1}{8}$ in. apart on the prepared surface. The sample is then immersed in a saturated solution of mercuric chloride for about 30 sec. During this time, mercury deposits upon the exposed aluminum along the scratches. The sample is then removed and placed in a dish of distilled water. The deposited mercury dissolves the aluminum at the interface and thus undermines the oxide film. The small squares of film float free from the aluminum after a short time and can be removed from the water bath with the specimen-supporting screens.

The quality of the oxide film formed by anodic oxidation in the disodium phosphate solution is illustrated by Figs. 5 to 9. No granular structure was detected in these films at magnifications of from 2,000 to 60,000 diameters. This is to be expected, from consideration of the manner in which this film forms. Evidently, this film grows to a limiting, barrier-layer thickness, after which growth stops because no pores develop.

USEFULNESS OF THE OXIDE-FILM METHOD

Like the replica methods, the oxide-film method is capable of faithfully reproducing the contour of the surface of the etched metallographic specimen. This is especially apparent in Figs. 5*c* and 5*d*, which represent the block structure of aluminum developed by deep etching. The image, however, is somewhat different from that obtained by the replica methods, as may

be seen from the schematic comparison of the methods shown in Fig. 1. Since the thickness of the oxide film is constant in the direction of growth—that is, normal to the original metal surface—parallel surfaces are represented by the same thickness of oxide, and thus appear with equal brightness in the electron image, analogous to the appearance of parallel surfaces in the optical image. This behavior is to be compared with that occurring with the replica methods, which represent parallel surfaces as areas of different brightness, dependent on the distances of the surfaces from some datum plane.

Contrast or differences in brightness in the electron image of the oxide film originate from differences in incident angle that the various plane elements of the structure make with the electron beam. As the angle between the surface element of the oxide film and the electron beam decreases, the distance through the film traversed by the electrons increases, and the intensity of the electron image decreases. Thus, surface elements normal to the electron beam appear bright, those parallel to the electron beam appear black, and those at intermediate angles appear various shades of gray, as shown in Fig. 5c.

The action of constituent particles—particles of a second phase formed from the melt or precipitated from solid solution—during the formation and removal of the oxide films provides an advantage of the oxide-film method over the replica methods. During the anodic oxidation of aluminum alloys, some of the microconstituents are readily oxidized or dissolved, some are more slowly oxidized, and others are not oxidized but are left unattacked.³¹⁻³³ Consequently, the oxide film may contain occluded particles of the unchanged constituents as shown in Fig. 3; it may contain occluded oxidation products of the constituent or it may contain holes corresponding to the constituent particles. In all cases, evidence of constituent particles is apparent

in the electron image as shown in Fig. 1 regardless of whether or not the particles are etched below the general surface level of the sample.

The principal advantage of the oxide-film method is realized when the constituent particles or their oxidation products are left embedded in or affixed to the oxide film as indicated schematically in Fig. 4. Under these conditions the contrast in the electron image will not only be controlled by differences in thickness of the oxide but also by the difference in electron-scattering ability of the aluminum oxide and the embedded or affixed particles. Since the ability to detect fine particles by the electron image depends upon the difference in brightness between the image of the particle and the background, the oxide-film method should be capable of revealing finer particles than are revealed by the replica methods, which are dependent upon thickness differences alone for image contrast.

RESULTS OBTAINED BY THE OXIDE-FILM METHOD

Block Structure

Structures developed by deep-etching metals have provided an interesting subject for the electron microscope.^{2,5,10,12,13,16} Under suitable conditions, deep etching of aluminum in solutions containing hydrochloric acid and hydrofluoric acid first causes the formation of the familiar cubic etch pits shown in the electron micrograph in Fig. 5a. Continued etching provides additional exposure of the cube faces, until the original metal surface is entirely removed. In this condition, shown by Figs. 5b to 5d, the structure appears to be composed of stacked blocks having surfaces composed of planes parallel to the cube planes of the lattice.

The usefulness of the electron microscope in examining the block structure developed by deep etching is well demon-

strated by the comparison of the photomicrograph in Fig. 5*b* with the electron

micrograph in Fig. 5*a* within the grains and at the grain boundaries of the deep-etched sample, shown



FIG. 5.—STRUCTURES OF DEEP-ETCHED SAMPLES OF ANNEALED 0.9 PER CENT SILICON-ALLOY SHEET
a. Electron micrograph of cubic etch pits. $\times 4000$.
b. Optical photomicrograph of cubic block structure. $\times 500$.
c. Electron micrograph of cubic block structure within a single grain. $\times 8000$.
d. Electron micrograph of structure adjacent to grain boundary. $\times 8000$.

micrographs in Figs. 5*c* and 5*d*. In addition to revealing details finer than those resolvable with the optical microscope, the electron microscope is also capable of clearly focusing the different levels

partly out of focus in the optical photomicrograph. This is possible because of the relatively great depth of focus of the electron microscope as compared with that of the optical microscope.

The nature of the cubic structure developed by deep-etching aluminum is not clearly understood. The cubic pattern is regular only in the sense that the faces

of the structures developed by deep etching, which can be obtained only by use of the electron microscope, will be fundamental in fully comprehending the cold-

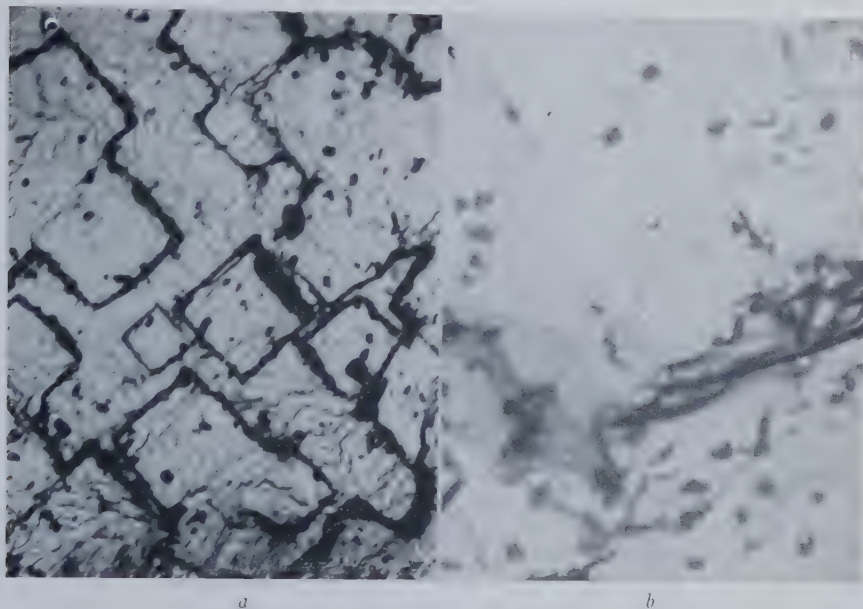


FIG. 6.—STRUCTURES OF DEEP-ETCHED SAMPLES.

a. Block structure of annealed commercial 1.25 per cent manganese-alloy sheet. $\times 4000$.
b. Structure of hard-rolled 1.23 per cent silicon-alloy sheet. $\times 16,000$.

developed form three sets of roughly parallel planes in each grain. The size of the blocks and their general shape vary considerably. Although the alignment of the blocks in a given grain is fairly constant, there are indications of slight orientation differences, which may account for this type of etching behavior. With some alloys, like the commercial wrought aluminum alloy 3S, which contains 1.25 per cent manganese, the cubic faces may contain a fine structure of a more or less random pattern as shown in Fig. 6*a*. In cold-worked samples the block structure is not cubic but nonuniform, as shown in Fig. 6*b*. Nonuniform block structures have been reported for aluminum in the cast and cold-rolled conditions whereas cubic block structures have been found only for annealed material.¹⁶ Complete knowledge

of the structures developed by deep etching, which can be obtained only by use of the electron microscope, will be fundamental in fully comprehending the cold-

Precipitation from Solid Solution

The electron microscope should be capable of providing much useful information on the size and distribution of the precipitate particles during the early stages of aging—information that can only be inferred from other types of examination. Although the optical microscope reveals indirect evidence of precipitation in aluminum alloys in the early stages of aging and at low aging temperatures,³⁴⁻³⁷ the platelike shape of the precipitate particles can be optically resolved only after relatively long aging periods or in samples aged at relatively high tempera-

tures.³⁵ Theoretically, the electron microscope should be capable of resolving the precipitate particles when they are platelets only 10 Å. or less in thickness and

tron micrographs show the precipitate and the structure developed by deep etching in two samples of 3S alloy sheet fabricated by two different practices. The

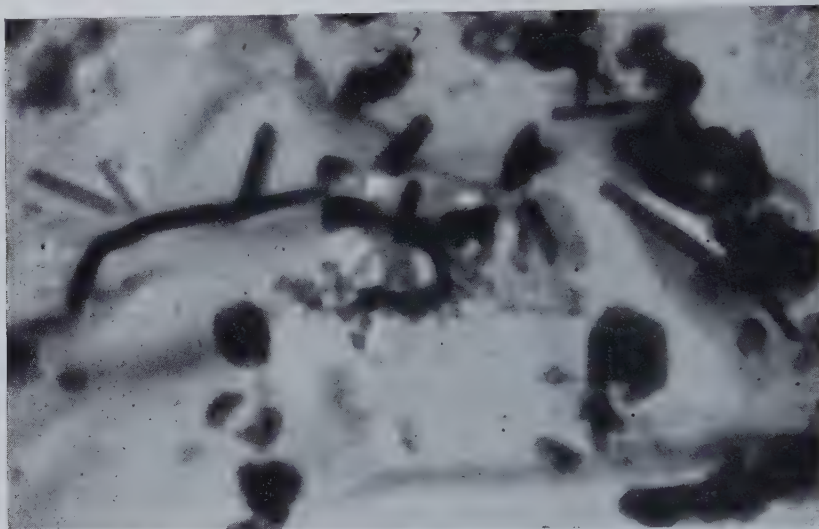


FIG. 7.—WELL-DEVELOPED PARTICLES OF SILICON PRECIPITATE IN DEEP-ETCHED 1.23 PER CENT SILICON-ALLOY SAMPLE. $\times 40,000$.

before they have grown in thickness sufficiently to diffract X-rays as three-dimensional crystals.³⁶

The appearance of the precipitate as portrayed by the oxide-film method varies with the nature of the precipitating constituent as well as with the manner of preparation of the sample. Constituents such as Si and $MnAl_6$, which are not dissolved or oxidized during the anodic treatment, appear as dense, black particles of a characteristic shape in or on oxide films from deep-etched samples, as shown in Figs. 6*b*, 7, 8*a* and 8*b*. Particles of silicon, which are probably platelike in shape, are shown in Fig. 6*b*. An electron micrograph of another area of this sample is shown in Fig. 7, where the silicon particles appear as six-sided plates in a number of different orientations. The optical microscope gives no indication of this shape because of its limited power of resolution. This is also true of the precipitate shown in Figs. 8*a* and 8*b*. These elec-

tron micrographs show the precipitate and the structure developed by deep etching in two samples of 3S alloy sheet fabricated by two different practices. The

one sample shown in Fig. 8*a* contains constituent particles considerably larger than those in the other sample shown in Fig. 8*b*. This difference in size of the submicroscopic constituent particles first revealed by the electron microscope is considered responsible for pronounced differences in the characteristics of these two samples. The precipitate particles that are not oxidized during the formation of the oxide film may appear as outlined areas in photomicrographs of oxide films from metallographically polished and etched samples, as shown in Figs. 8*c*, 8*d* and 9. In Figs. 8*c* and 8*d* electron micrographs are shown of oxide films from polished and etched samples of the same two lots of 3S sheet shown in the deep-etched condition in Figs. 8*a* and 8*b*. The flat constituent particles evidently are undermined during the etching treatment, and they fall out of the surface to leave cavities in the aluminum. This type of behavior is observed with the optical

microscope when the particles are larger. During the anodic oxidation treatment, the side walls and bottoms of the cavities

shows the influence of the aging temperature upon the particle size of the MnAl_6 precipitate formed during 16 hr. aging time

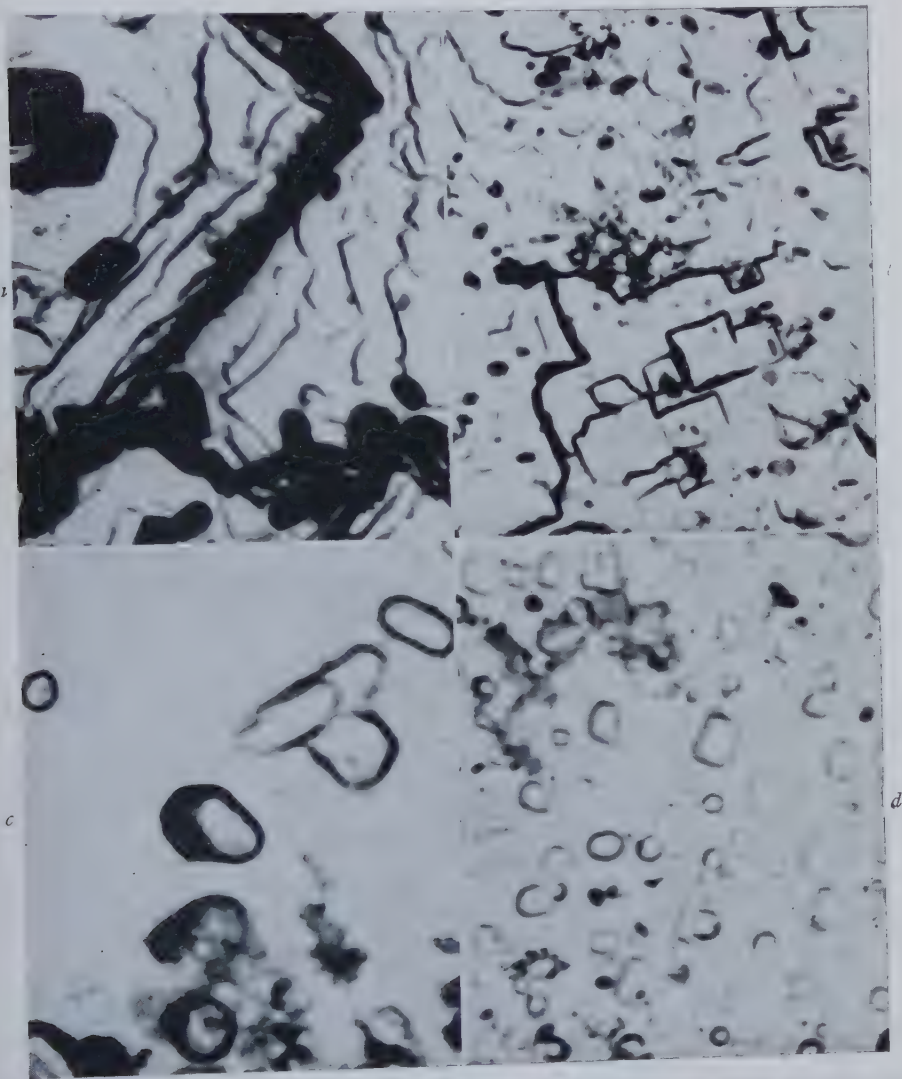


FIG. 8.—FINE CONSTITUENT PARTICLES IN ANNEALED COMMERCIAL 1.25 PER CENT MANGANESE ALLOY SHEET.

a and *b*. Structures of deep-etched samples of sheet made by two different practices. $\times 16,000$.
c and *d*. Structures of metallographically polished and etched samples of same material shown in *a* and *b*, respectively. Etched with 0.5 per cent HF. $\times 16,000$.

receive a thin oxide film, as does the general surface, and the presence of the precipitate is evidenced by the outlined cavities shown in Figs. 8 and 9. The latter

in a high-purity aluminum-manganese alloy containing 1.08 per cent Mn. The precipitates in samples of two other compositions aged in a similar way also appear

as outlined areas of which the average size depends upon the aging temperature. The size of the outlined areas in the three sets of

similarity of the size and distribution of the outlined areas in Figs. 8*c* and 8*d* to the MnAl_6 particles in Figs. 8*a* and 8*b* is

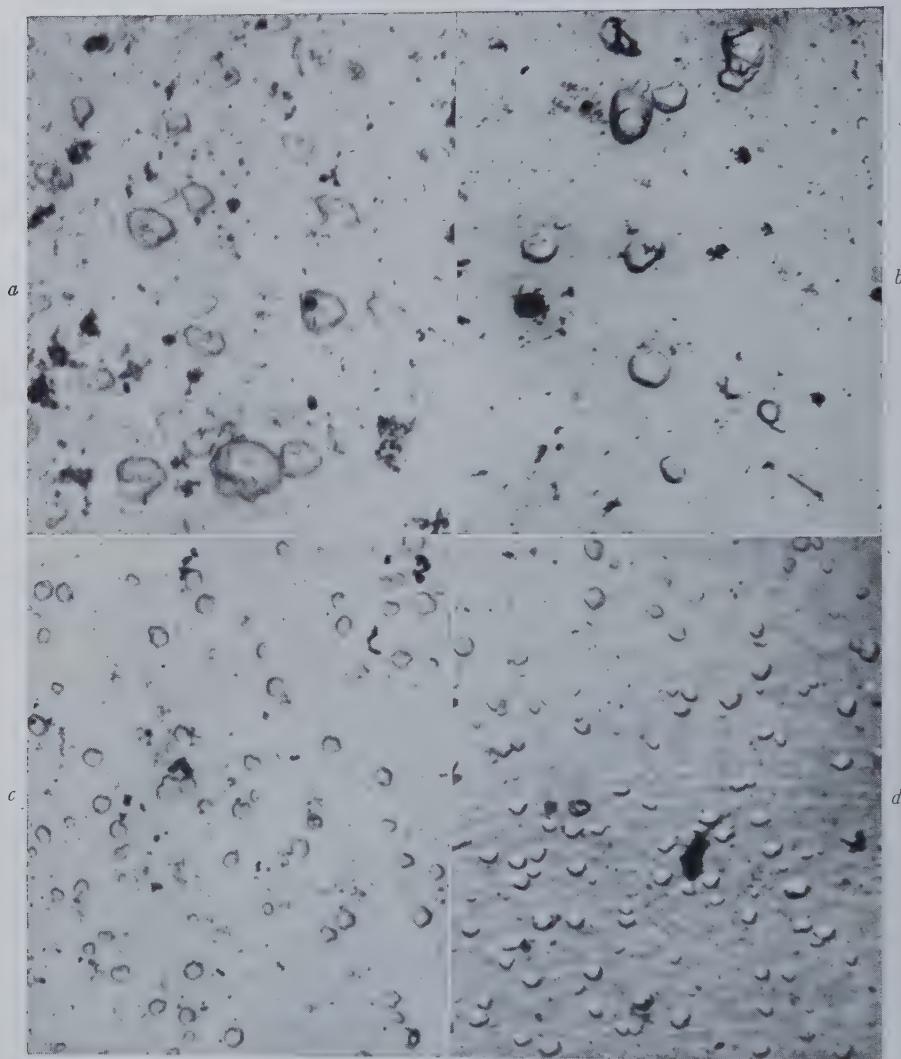


FIG. 9.—PRECIPITATION IN 1.04 PER CENT MANGANESE ALLOY SOLUTION HEAT-TREATED AND AGED. Polished samples etched with 0.5 per cent HF. $\times 4500$.

- a. Aged 16 hours at 450°C .
- b. Aged 16 hours at 400°C .
- c. Aged 16 hours at 350°C .
- d. Aged 16 hours at 300°C .

samples varies with temperature and composition in a manner consistent with the laws of precipitation. This fact and the

good evidence that the outlined areas actually represent precipitate particles.

When the precipitate particles are rela-

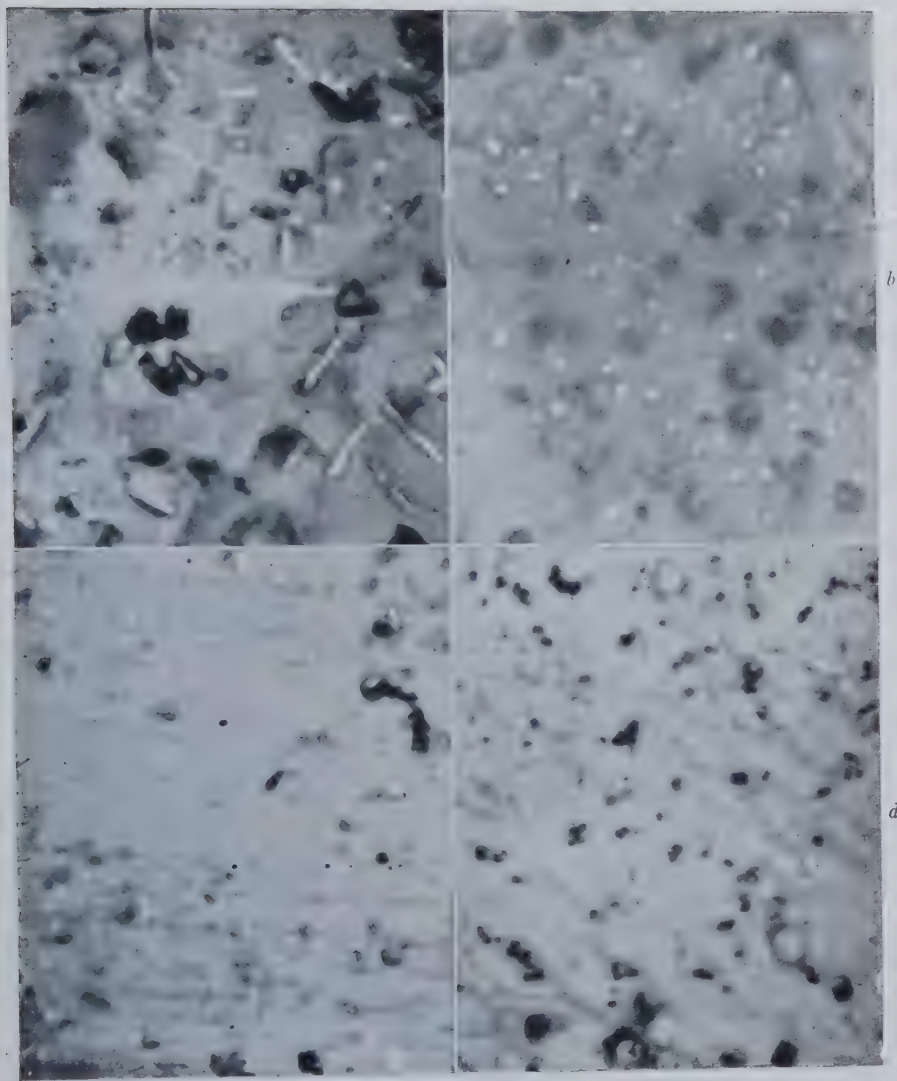


FIG. 10.—PRECIPITATION IN VARIOUS ALUMINUM ALLOYS.

- a. Alloy containing 1.23 per cent silicon solution-heat-treated and then aged 16 hr. at 215°C. Oxide film formed on electropolished sample in ammonium borate electrolyte. $\times 20,000$.
- b. Alloy containing 25 per cent zinc solution-heat-treated and then aged 46 days at 100°C. Oxide film formed on deep-etched sample in ammonium borate electrolyte. $\times 40,000$.
- c. Commercial alloy containing magnesium, silicon and chromium solution-heat-treated and aged. Oxide film formed on polished sample in ammonium borate electrolyte. $\times 20,000$.
- d. Same material as c. Oxide film formed on electropolished sample in borax-boric acid electrolyte. $\times 20,000$.

tively large and anchored deep into the matrix (compared with the thickness of the oxide film), as in a Widmanstätten pattern with plates at an angle to the plane of polish, the precipitate usually appears as white streaks corresponding to holes in the oxide film left by the cross sections through the precipitate plates. With constituents such as silicon, which are not oxidized or dissolved during the anodic treatment, the particles form discontinuities in the oxide film, and the film may be pulled from the particles to leave holes in the film. This might occur during the film-removal process if the film were freed from the aluminum before the mercury had freed the constituent particles from the aluminum. Such a case is represented by Fig. 10a, which shows a Widmanstätten pattern of holes left by silicon particles in an oxide film from an aged aluminum-silicon alloy. Similar patterns of streaklike holes are also observed with aged aluminum-copper, aluminum-silver and other alloys in which the precipitate appears in a somewhat coarse Widmanstätten pattern and the constituents are oxidized or dissolved during the anodic treatment to leave gaps in the oxide film.

When the precipitate particles are small, they may appear either as black particles or as white holes, depending upon whether or not the constituent is oxidized and dissolved during the oxidation treatment. This factor depends not only upon the nature of the constituent but also upon the conditions of the anodic oxidation treatment. Electron micrographs of oxide films formed by two different anodic treatments on the commercial aluminum-magnesium-silicon alloy 53S in the heat-treated and aged condition are shown in Figs. 10c and

10d. The constituents appear as black particles in the film formed in the borax-boric acid solution using a potential of 30 volts (Fig. 10d), while some appear as white holes in the film formed in the ammonium borate electrolyte using a potential of 50 volts (Fig. 10c). Similar white holes, probably corresponding to oxidized or dissolved precipitate particles that are exposed during the oxidation treatment, are observed also in films formed by the ammonium borate process on aluminum-magnesium and aluminum-zinc alloys, as shown in Fig. 10b. The larger, more or less outlined areas in Fig. 10b may be oxide-coated cavities in the matrix left by the zinc precipitate particles exposed and dissolved during the deep etching.

RESULTS OBTAINED BY THE REPLICA METHODS

Although the oxide-film method is found in general to be very satisfactory for the study of aluminum alloys with the electron microscope, occasionally one of the replica methods can be used to advantage in spite of the increased time and work involved. With this view in mind, a few results obtained by the formvar and the polystyrene-silica processes are presented in Figs. 11 and 12. Precipitation in a high-purity aluminum-copper alloy aged at 250°C. is shown in Fig. 11. Localized precipitation along slip-plane traces³⁴ is evident in the optical photomicrograph in Fig. 11a for the sample aged 30 min.; however, the CuAl_2 particles cannot be clearly resolved with the optical microscope until after the sample has been aged for more than 24 hr. at this temperature (see Fig. 11f). Electron micrographs of formvar films

a. Optical photomicrograph of sample aged $\frac{1}{2}$ hour. Polished sample etched in HF-HCl-HNO_3 . $\times 100$.

b. Electron micrograph of formvar replica from same sample. Electropolished. $\times 20,000$.

c. Electron micrograph of formvar replica from sample aged 2 hours. Electropolished. $\times 20,000$.

d. Electron micrograph of formvar replica from sample aged 24 hours. Electropolished. $\times 20,000$.

e. Electron micrograph of silica replica from same sample. $\times 5,000$.

f. Optical photomicrograph of same sample. $\times 500$.

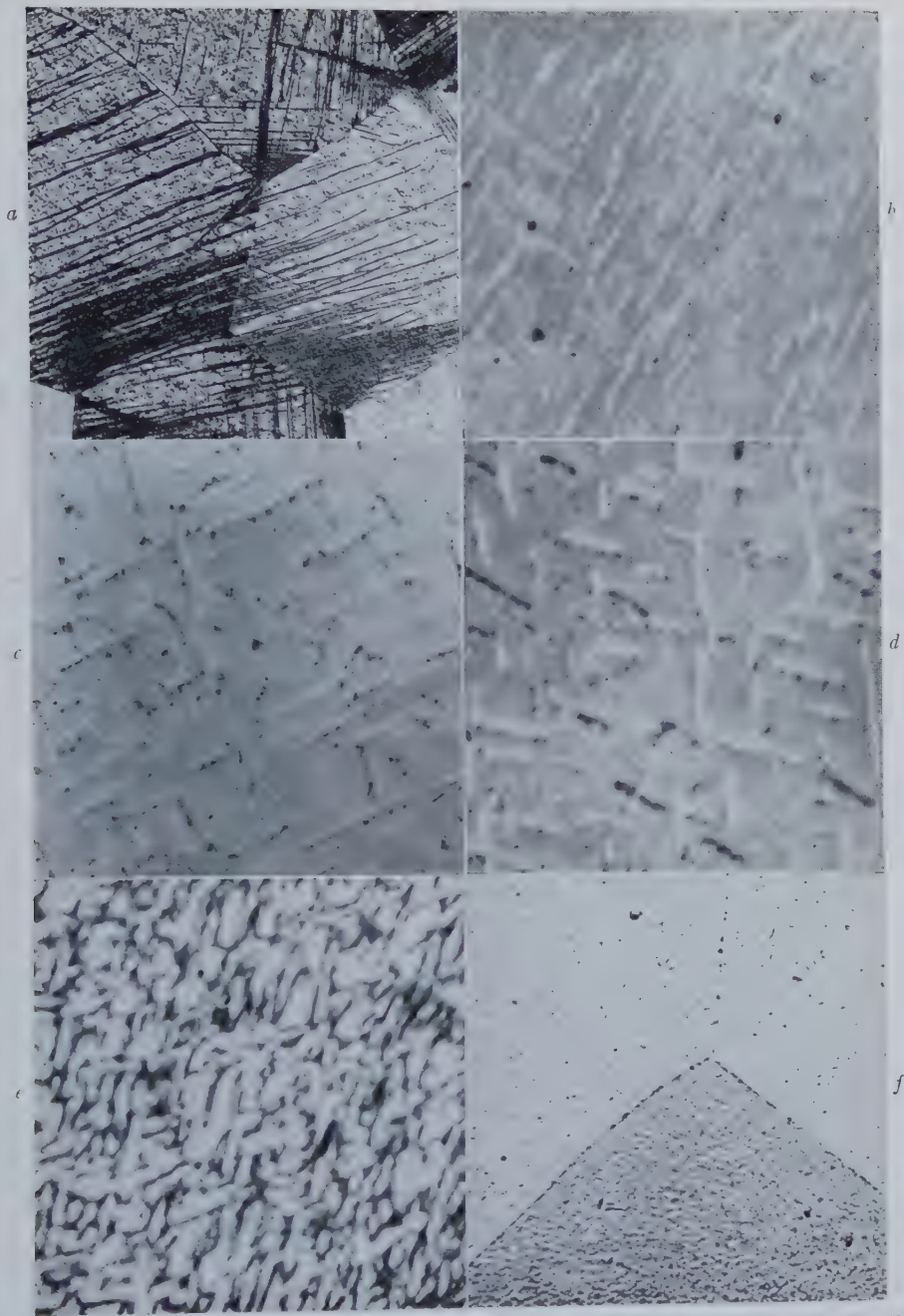


FIG. 11.—PRECIPITATION IN 4.5 PER CENT COPPER ALLOY SOLUTION HEAT-TREATED AND THEN AGED AT 250°C .

For remainder of legend see opposite page.

mechanically stripped under water* from the aluminum-copper alloy samples aged for various time periods are shown in Figs. 11*b* to 11*d*. The Widmanstätten pat-

remaining illustrations. An electron micrograph of a silica replica from the same sample used for Fig. 11*d* is shown in Fig. 11*e*. The individual precipitate par-

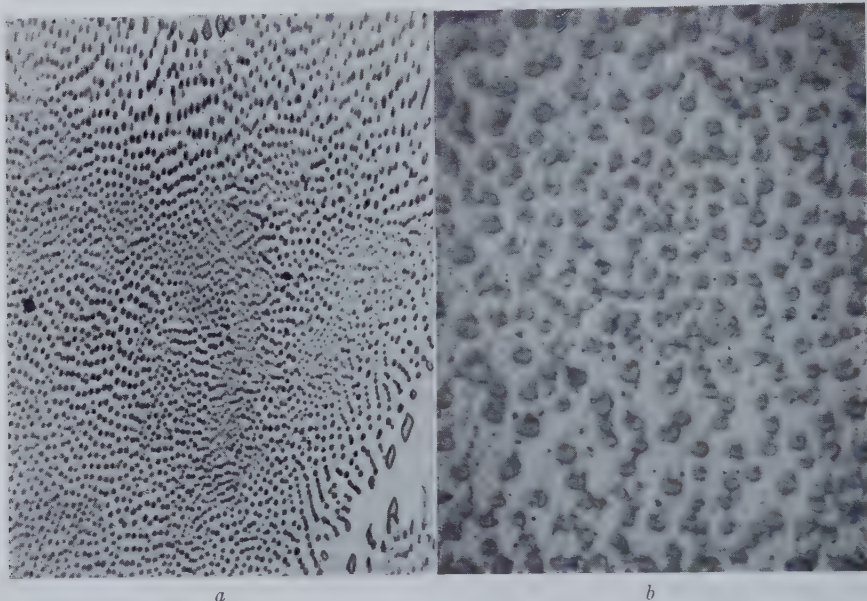


FIG. 12.—STRUCTURE OF EUTECTIC IN CHILL-CAST 3.5 PER CENT IRON ALLOY.

Polished sample etched with 0.5 per cent HF.

a. Optical photomicrograph. $\times 1,500$.

b. Electron micrograph of silica replica. $\times 4,000$.

tern of precipitate particles and the growth of the particles during aging are evident.

The true negative replica is represented by Fig. 11*b*, where the CuAl_2 particles left in relief appear as white cross sections through plates because of the smaller thickness of the replica at these particles. The replicas shown in Figs. 11*c* and 11*d* may be classed as modified negative replicas, because many of the white streaks representing the CuAl_2 plates have a deposit of etching products that reverse the tone contrast between the precipitate and the matrix.

Two applications of the polystyrene-silica method are demonstrated in the

ticles and the Widmanstätten pattern are not as distinct as those shown in Fig. 11*d* but are more clearly resolved than the structure visible with the optical microscope as shown in Fig. 11*f*. A fine eutectic structure of FeAl_3 and aluminum is shown in Fig. 12. The optical microscope resolves the particles in the coarser part of the structure as shown in Fig. 12*a* but the shape and boundaries of the finer particles are apparent only on examination with the electron microscope.

CONCLUSIONS AND SUMMARY

The results obtained in revealing the fine structure of various aluminum alloys by employing the electron microscope are considered encouraging. Many of the structures shown in this paper are far beyond resolution by the optical micro-

* The formvar films may also be stripped from aluminum samples using the mercury method as used to strip oxide films. Mahl has used this method to strip lacquer films.^{4,11,12}

scope. Available methods for preparing specimens such as the oxide film, formvar replica and silica replica are compared and the results illustrated. A new method for preparing structureless anodic oxide films for use as electron microscope specimens is described in detail. In most instances the results obtained with the new method are considered better than those possible with the older methods. Further research is in progress to extend the application of the electron microscope for the investigation of submicrostructures of aluminum alloys.

ACKNOWLEDGMENT

The authors wish to thank Mr. W. H. Gitzen for his collaboration in the use of the electron microscope in the Chemical Development Division of Aluminum Research Laboratories at East St. Louis, Illinois.

They are indebted also to Dr. R. F. Mehl and Dr. C. S. Barrett for permission to use the electron microscope at the Carnegie Institute of Technology.

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DISCUSSION

(W. A. Dean presiding)

C. F. BARRETT, JR.* Teterboro, N. J.—What amount of distortion occurs in removing these replicas from the surface of the original sample?

A. H. GEISLER (author's reply).—In general, no evidence of any distortion has been observed in oxide films which might have been produced during their removal from the metal surface. This is to be expected, since a chemical removal process is employed in contrast to the mechanical removal processes used in some of the replica techniques. In the close vicinity of the scratches inscribed on the oxidized sample, to cut the oxide film into squares, naturally some distortion of the metal sample occurs, but these areas seldom fall within the field on the supporting screen that is examined in the electron microscope.

M. L. FULLER,* Palmerton, Pa.—I would like to offer a suggestion regarding the terminology. The science of controlling the trajectories of electrons in a vacuum is known as electron optics. It follows, therefore, that the electron microscope is an optical instrument, as well as the conventional microscope. My suggestion is that we designate the two instruments as "light microscope" and "electron microscope," rather than optical microscope and electron microscope; that we term the two micrographs "photomicrograph" and "electron micrograph," rather than photomicrograph and electron photomicrograph.

C. S. BARRETT,† Pittsburgh, Pa.—The anodic oxide replicas seem to be excellent for showing the deep-etched structure of aluminum alloys, which are particularly difficult samples to handle with the polystyrene silica method.

I should like to suggest that there might be opportunities for misinterpretation of oxide replicas when they are used to count the number of precipitated particles per unit area of the surface. Is it not possible that an oxide film contains not only the particles trapped within it but also some particles that floated around in the liquid after the metal was dissolved? Any particles that fell on the replica and remained there would, of course, be counted along with the ones that are within the film. Could this account for the difference in the number of particles in Figs. 10c and 10d?

A. H. GEISLER.—It is possible that constituent particles loosened from the aluminum matrix during the film-removal process and unattached to the oxide film might be picked up on the film from suspension in the water bath; however, careful washing of the oxide film should remove these if a determination of particle number is desired rather than particle size and shape alone. In investigations of the latter features and in electron-diffraction studies, some such particle-concentrating scheme might be advantageous.

I do not believe that there is any real difference in the number of particles repre-

* Research Division, New Jersey Zinc Company.

† Metals Research Laboratory, Carnegie Institute of Technology.

* Eclipse-Pioneer Division of Bendix Aviation Corporation.

sented in Figs. 10c and 10d if the white areas, faintly visible in Fig. 10c and corresponding to holes left in the oxide film by particles oxidized and dissolved in the film formation treatment, are counted in addition to the black particles. We know that the conditions of anodic oxidation determine whether or not a particular constituent is oxidized and dissolved by the electrolyte or is left unattacked in the oxide film. This is demonstrated by Figs. 10c and 10d, where one anodic oxidation treatment has left all the constituents or their oxidation products in the aluminum-oxide film, as shown by Fig. 10d, but a different oxidation treatment has resulted in complete removal of some of the constituents or their oxidation products to leave the white holes in the aluminum-oxide film shown in Fig. 10c.

C. S. BARRETT.—Do you think that Fig. 2a might have any particles picked up from the liquid?

A. H. GEISLER.—Yes, but I do not think that they are all constituent particles from the alloy. I think that some of the large black particles in Fig. 2a are particles of a hydrated alumina, which under certain conditions may form during the film-removal operation. Some of the spurious material may also be particles of residual aluminum. Mahl¹² and Fischer and Kurz³⁰ have taken precautions to remove both these materials by washing the oxide films in dilute hydrochloric acid after removal from the aluminum. We have not considered this necessary, since it is usually possible to find many areas of the films that have no spurious material and that appear to be representative of the microstructure of the sample.

G. E. PELLISSIER, JR.,* New York, N. Y.—Do the authors feel that the top surface

of the oxide coating follows the contour of the surface or is the top surface smooth? In Fig. 10a, might not there be some ambiguity about the interpretation of the light areas?

A. H. GEISLER.—There is no doubt that the top surface of the oxide film follows the contour of the samples as represented in Fig. 1. If the top surface were smooth, parallel surfaces at different levels in the microstructures such as those depicted in Figs. 5c and 5d would not appear with equal brightness but would have different brightnesses, depending on the distance of the surface from some datum plane, as with the replica methods. The light areas in Fig. 10a cannot be attributed to anything other than holes in the oxide film, probably where relatively large silicon particles had been located in the sample.

MEMBER.—I should like to ask about 12b. It has been indicated that in the silica replica process one surface would be flat, yet those particles all have a black edge around them.

A. H. GEISLER.—Whether the top surface of a replica is flat or follows the contour, I think depends upon the magnitude of the detail and change in contour present on the surface of the metal sample. With microstructural features of the size shown in Fig. 12b, where a distance of 4 mm. represents 1μ , the top surface of the replica follows the contour to some extent over most of the particles represented. On the other hand, with much finer microstructural features, such as those represented in Fig. 1, where a distance of 44 mm. represents 1μ , the top surface of the replica is probably smooth as shown. This explanation is in agreement with results with silica replicas published by Heidenreich.²⁸ Our observation with formvar replicas, however, indicates that the top surface remains flat over larger contour changes than does the top surface of silica replicas.

* Columbia University.

Orientations in Diffusion Layers

By SHUELING WOO,* CHARLES S. BARRETT,† MEMBER AND ROBERT F. MEHL,‡ MEMBER A.I.M.E.

(New York Meeting, February 1944)

WHEN one solid phase is generated from another, fixed and rational orientation relationships are observed to subsist between the parent and the new crystal. The principle has been proposed¹ that the relationships obtaining between the same two phases are identical whatever the type of phase change involved, or whichever of the phases may act as parent. Many types of phase changes have been studied: allotropic transformations in pure metals, precipitation from solid solutions, eutectoid decompositions, peritectic reactions, the formation of oxide layers, and others.²

Phase layers generated by diffusion of one metal into another constitute an additional type of reaction. This report provides new data on the orientation relationships occurring between phase layers formed by diffusion, in the Cu-Zn system,[§] and furnishes further evidence in support of the principle.

MATERIALS AND METHODS

The Cu-Zn system is especially suitable for these studies since the high vapor pres-

sure of Zn provides an opportunity readily to create one phase poorer in Zn upon a parent phase richer in Zn by removing Zn by vaporization, or to reverse this process by adding Zn from Zn vapor; e.g., the beta phase can be found as a layer upon gamma by dezincing, or gamma can be found on beta by addition of Zn from Zn vapor. Since orientation relationships are to be sought, requiring crystals large enough for orientation determinations, it is convenient to prepare single crystals or large grains of the parent phase.

The samples were prepared from oxygen-free high-conductivity copper and Horse Head zinc by melting under a borax flux in a graphite crucible. Large crystals of beta brass were grown by the strain-anneal method, in plates sectioned from the cast ingots, by the following procedure. Rockwell-hardness indents were made at 1 cm. intervals and with various loads, then the plates were annealed for 4 days at 700°C. in Nichrome boxes packed with beta-brass chips and graphite. Surface layers were removed by grinding and etching to a depth of about 1.0 mm., and individual grains were cut out. Crystals of alpha and gamma brass were prepared by freezing, by lowering a graphite crucible at speeds less than one inch per hour through a furnace held at a constant temperature above the melting point. Single crystals were cut out with a jeweler's saw, ground, polished and etched. Care was taken to remove cold-worked layers from the finished crystals

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* Division Chief, National Resource Commission Machine Works, Kunming, China; formerly graduate student Department of Metallurgical Engineering, Carnegie Institute of Technology, Pittsburgh, Pennsylvania.

† Associate Professor of Metallurgical Engineering, and member of staff, Metals Research Laboratory, Carnegie Institute of Technology.

‡ Professor of Metallurgical Engineering and Director of the Metals Research Laboratory, Carnegie Institute of Technology.

¹ References are at the end of the paper.

[§] Some of the present results were noted in brief six years ago; see ref. 1.

by etching, in order to minimize the danger of recrystallization.

The compositions of the alpha, beta and gamma alloys were 70.0 per cent Cu, 30.0

matrix. The reflections from each phase were identified by the reflection angles and by the shape of the spots on the film, and the relative orientation of the phases



FIG. 1.—SECTION THROUGH RIM OF BETA AND CORE OF ALPHA AFTER DIFFUSION AT 700°C. $\times 7$.

per cent Zn; 53.4 per cent Cu, 46.6 per cent Zn; and 33.3 per cent Cu, 66.7 per cent Zn, respectively.

To produce the desired alloy layers on the surface by diffusion, each crystal was placed in a loose-fitting perforated box of brass having the composition of the layer that was to be produced, and the box, in turn, was embedded in chips of this same composition. Thus, for example, a crystal of beta brass was placed in a box of alpha brass and surrounded by alpha-brass chips. The crystal, box, and chips were then all sealed in evacuated Pyrex or silica tubes with a small amount of graphite and heated in furnaces controlled to $\pm 5^\circ\text{C}$. This arrangement provided a large surface area of the alpha composition to which the zinc vapor could diffuse from the beta crystal until the surface of the latter reached the alpha composition. After the diffusion treatment, each sample was quenched in iced brine, to avoid precipitation, and was cut, ground or etched so as to reveal the matrix together with the layer produced by diffusion.

X-ray photograms of the Davey-Wilson type³ were prepared with a beam of Cu K α radiation striking both phases at the interface between the diffusion layer and the

was determined by plotting on stereographic projections using a Wulff net 15 $\frac{3}{4}$ in. in diameter. In certain samples the diffusion layer contained crystallites differing in orientation among themselves 3° to 6° ; for these, the center of gravity of the cluster of spots was treated as the reflection from a single crystal. In some cases of this type the solution was checked by also solving the orientation of one crystallite of the group. Errors in reading and plotting the films probably do not exceed 2° and usually are less than 1° .

Microscopic examination of the samples showed that in none of the experiments reported in this paper was there precipitation in any of the phases on cooling from the diffusion temperature to an extent that interfered with the interpretation of the X-ray photograms; in fact, only one of the samples contained enough precipitate to be detectable on the photograms. A photograph of this sample is shown in Fig. 1; the rim of beta surrounding the alpha core contains many precipitated crystals of alpha, but since the X-ray reflections from these were of lower intensity than the reflections from the core, it was not difficult to distinguish them in the diffraction patterns. It was possible to analyze

the orientations of five grains in this rim, avoiding a portion of the rim that was recrystallized.

When alpha was formed on beta at

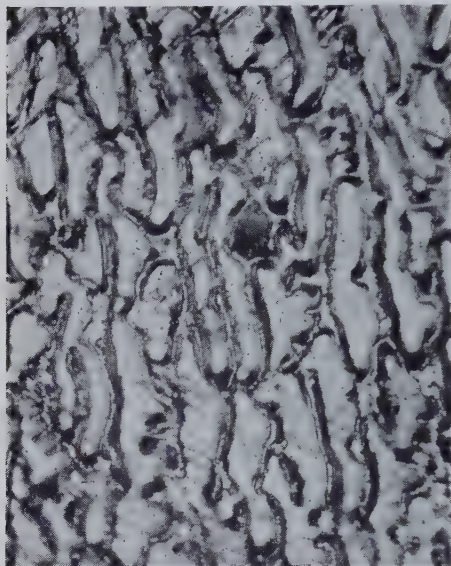


FIG. 2.—SURFACE OF ALPHA PHASE FORMED ON CORE OF BETA AT 700°C. WITHOUT POLISHING OR ETCHING. $\times 300$.

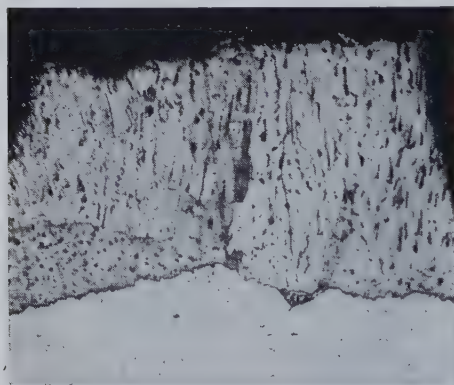


FIG. 3.—SECTION THROUGH RIM OF ALPHA (GRAY) CONTAINING CHANNELS AND CORE OF BETA (WHITE), AFTER DIFFUSION AT 700°C. ETCHED WITH H_2O_2 IN NH_4OH . $\times 75$.

700°C., the surface developed the network of grooves shown in Fig. 2. The interior became perforated with hollow channels, showing as black dots and threads in Figs.

3 and 4, which appear to extend in crystallographically determined directions. These must result from the volume shrinkage that accompanies the loss of zinc in

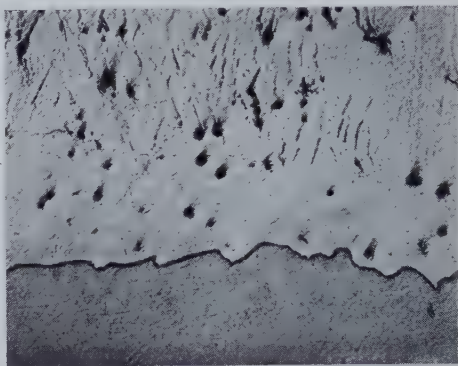


FIG. 4.—SAME SPECIMEN AS FIG. 3, ETCHED WITH HNO_3 ; CHANNELS IN ALPHA PHASE (TOP) SHOW PREFERRED DIRECTIONS. $\times 200$.

the formation of alpha, and is analogous to the cracking of oxide films that are denser than the parent metal on which they form.

Cracking and recrystallization (with resultant loss of fixed orientations) of the layer formed by diffusion became a problem only when gamma was formed on beta at 550° and at 500°. Near the beta-gamma interface, however, a sound layer of gamma was found (see Fig. 5) and it was possible to grind away the outer portion of the rim of gamma so that only the sound portion remained, and this alone was used for X-ray measurements.

RESULTS

When the relative orientations of a crystal and its diffusion layers had been determined, a plot was made showing poles of the low-indices planes $\{001\}$, $\{110\}$, and $\{111\}$ of the new phase on a standard stereographic projection of the matrix crystal. These poles were then rotated into a single unit triangle of the standard projection of the matrix crystal, using the rotation axes of symmetry of the matrix. A separate plot was made

for each set of poles in each series of experiments.

The formation of beta from alpha was produced by the diffusion of zinc vapor

all experiments are summarized in Table 1.*

It is convenient to describe the orientation relationships found in terms of the



FIG. 5.—SECTION THROUGH RIM OF GAMMA FORMED ON CORE OF BETA (LOWER RIGHT) AT 550°C. $\times 100$.

Showing sound layer of gamma just above darkly etched core, adjacent to interface (black line). Surface material cracked and recrystallized into small grains. Glacial acetic etch.

from beta into a single crystal of alpha at a temperature of 400°C. for seven days; this produced nine large beta grains on various faces of the crystal; the orientations of all of these are combined in the unit stereographic triangles of Fig. 6. The upper triangle in this and succeeding figures is the pole figure for $\{100\}$ poles of the new phase, the middle is for $\{110\}$ and the lower is for $\{111\}$; the left-hand corner of each triangle is the pole of (100) of the parent or core crystal, the lower right corner is the pole of (110) and the upper right, (111) . The poles of crystals in the diffusion layers are shown as small dots.

Figs. 7 to 12 are similar stereographic projections covering the rest of the orientation determinations; the experimental conditions and the results obtained in

various ideal orientation relationships that have been proposed for transformations and Widmanstätten structures when body-centered cubic crystals form from face-centered cubic, or vice versa. These are listed in Table 2 and are plotted in the pole figures.

The first of these four is indicated in the pole figures by small open circles ($\circ$), the second by filled circles ($\bullet$), the third by crosses ($\times$), and the fourth by large open circles ($\bigcirc$).

Conclusions drawn from a comparison of these orientations and the plotted data are given in the last column of Table

* To complete the series of experiments a layer of epsilon was formed on a crystal of gamma by diffusing 72 hr. at 400°C.; the work was interrupted before the X-ray films from this sample could be analyzed.

1. It is shown that the orientations in Figs. 6 to 9 cluster about the Nishiyama and Kurdjumow-Sachs relationships, with greater scattering at the higher diffusion temperatures.

None of the experiments seem to confirm Bøggild's orientation, and there is little

sides of a single gamma crystal. An X-ray determination of this 650° experiment, however, is not available.

DISCUSSION OF RESULTS

The orientation relationships that occur between the alpha and beta phases in the

TABLE 1.—*List of Experiments and Summary of Results*

Results Plotted	Diffusion Layer	Parent Phase	Temperature of Diffusion, Deg. C.	Time of Diffusion, Days	Number of Grains Investigated	Type of Orientation Relationships
Fig. 6....	β	α	400	7	9 β , 1 α	Nishiyama
Fig. 7....	β	α	700	3	10 β , 2 α	Between Nishiyama and Kurdjumow-Sachs
Fig. 8....	α	β	500	1	11 α , 6 β	Between Nishiyama and Kurdjumow-Sachs
Fig. 9....	α	β	700	1.5	19 α , 7 β	Too scattered to distinguish type
Fig. 10....	γ	β	400	2	6 γ , 1 β	Identical orientations in two phases
Fig. 11....	γ	β	{ 550 500 }	{ 3 10 }	6 γ , 2 β	Identical orientations in two phases
Fig. 12....	β	γ	400	1.5	3 β , 1 γ	Identical orientations in two phases
	β	γ	650	1.5	1 β , 1 γ	Identical orientations indicated by indirect evidence

support for the fourth simple orientation listed—in fact, for the most sharply clustered data (Fig. 6) this fourth orientation is clearly incorrect. While this orientation has not been proposed in earlier orientation studies, it was thought advisable to include it in the interest of completeness.

Cu-Zn system have now been investigated for: (1) the precipitation of face-centered cubic alpha from body-centered cubic beta⁹⁻¹¹ (2) the formation of beta from alpha by the peritectic reaction,¹² and (3) the generation of beta from alpha and of alpha from beta in diffusion layers. In all these cases the orientations are the same—

TABLE 2.—*Ideal Orientation Relationships*

Type of Orientation	Parallel Planes	Parallel Directions	Key to Figs. 6-9
1. Kurdjumow and Sachs ⁴	(111) f.c.c. (110) b.c.c.	[1 $\bar{1}$ 0] f.c.c. [1 $\bar{1}$ 1] b.c.c.	○
2. Nishiyama ⁸	(111) f.c.c. (110) b.c.c.	[$\bar{2}$ 11] f.c.c. [$\bar{1}$ 10] b.c.c.	●
3. Bøggild ⁴	(100) f.c.c. (100) b.c.c.	[010] f.c.c. [011] b.c.c.	×
4.	(001) f.c.c. ($\bar{1}$ 10) b.c.c.	[$\bar{1}$ 10] f.c.c. [111] b.c.c.	○

Figs. 10, 11 and 12 indicate that the relation between beta and gamma is always one in which the cube axes in the two phases are parallel—i.e., the orientations of the two phases are identical—both when beta forms on gamma and when gamma on beta, independent of temperature. The final experiment listed in Table 1 also indicated this relation by the fact that a single continuous crystal of beta formed on all

they all lie close to the Kurdjumow and Sachs relationships, departing from this to some extent toward the Nishiyama relationship.

The orientation relationships that occur between the beta and gamma phases in the Cu-Zn system have been determined for: (1) the precipitation of complex b.c.c. gamma from b.c.c. beta,¹⁵ and, now, (2) the generation of gamma from beta and

of beta from gamma in diffusion layers. In these two cases the orientations are the

the principle that the orientation relationships obtaining between the same two

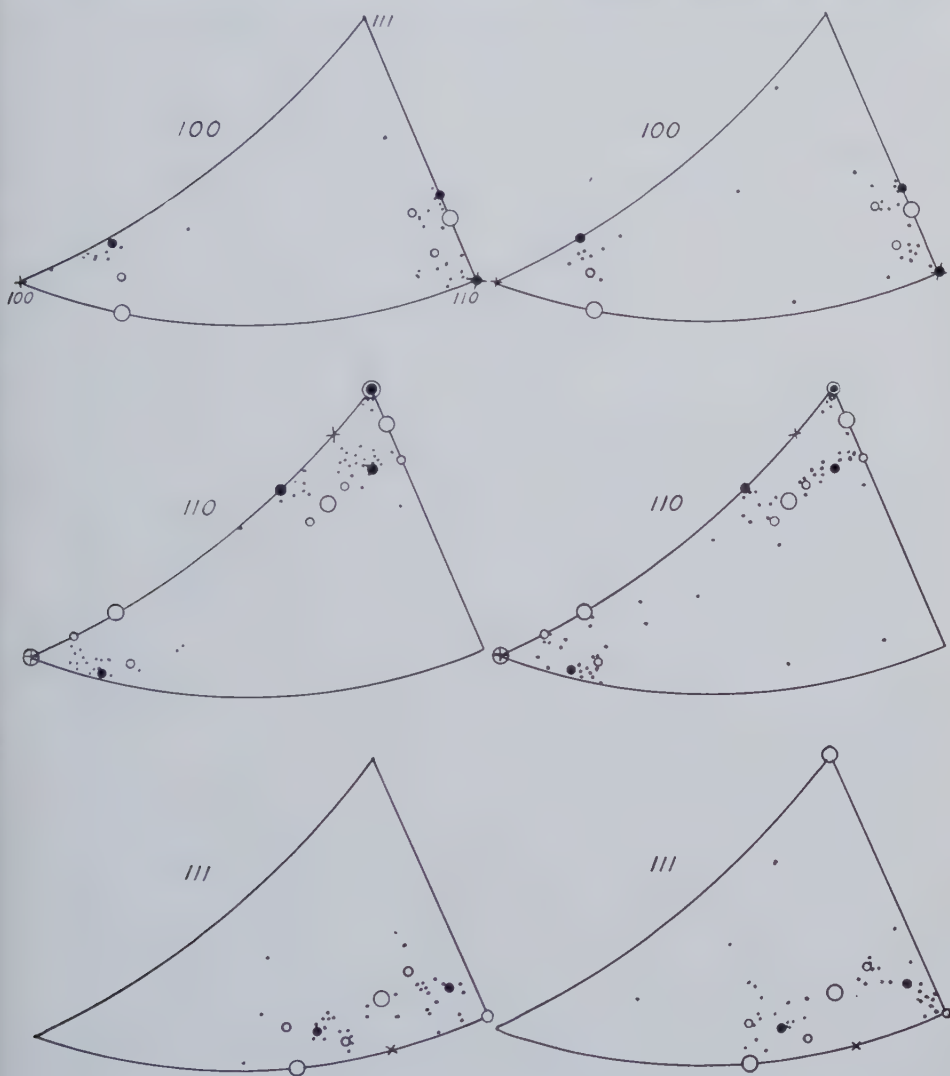


Fig. 6. At 400°C.

Fig. 7. At 700°C.

FIGS. 6 AND 7.—POLE FIGURES FOR ALPHA $\rightarrow$ BETA.

Orientation of diffusion layer shown by small dots in standard projection triangles of core crystal.

Upper triangle is (100) pole figure, middle triangle is (110) and lower is (111). See Table 2 for keys to symbols representing ideal orientations.

same, an orientation in which the cube axes in the two phases are parallel.

These data appear adequate to establish

phases are identical whatever the type of phase change involved. This principle applies whatever the direction of the reac-

tion, whichever of the lattices may act as parent. The identity in orientation relationships appears to originate in an identity in the nature of the process by which the

In the generation of beta brass from alpha by the inward diffusion of Zn, for example, we may picture the process as occurring in the following way: The addi-

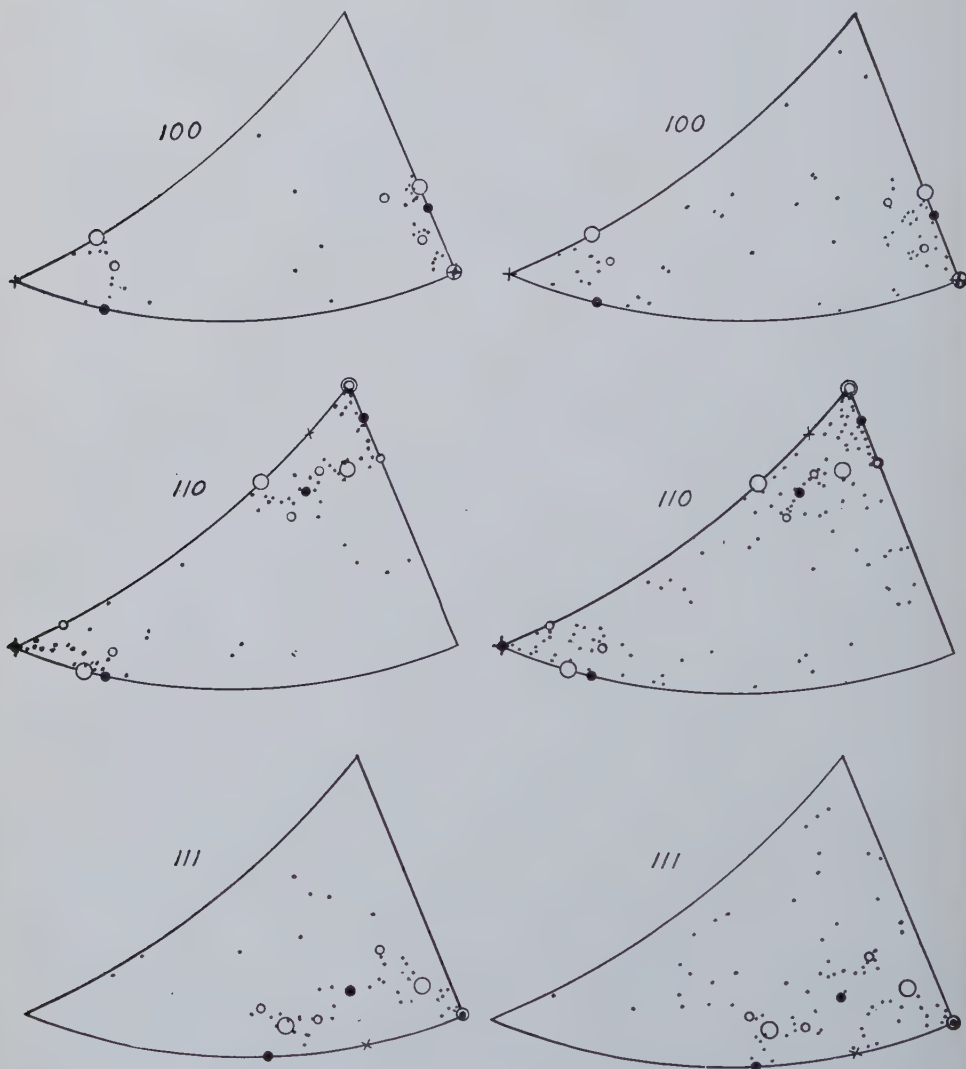


FIG. 8.—POLE FIGURES FOR BETA $\rightarrow$ ALPHA AT 500°C.

See Table 2 and caption of Fig. 6 for symbols.

FIG. 9.—POLE FIGURES FOR BETA $\rightarrow$ ALPHA AT 700°C.

new phase forms in all the types of reaction considered: in each case the new phase appears by nucleation in the lattice of the old.

tion of Zn produces a Zn concentration that rises from the original alpha composition at the core to the saturation

composition at the surface. The addition of Zn proceeds by the adsorption of atomic layers of Zn upon the surface, and their subsequent inward diffusion. This adsorp-

concentration fluctuations, characteristic of solid solutions, aid in the formation of such aggregates of atoms. These then transform to nuclei of beta in a manner wholly

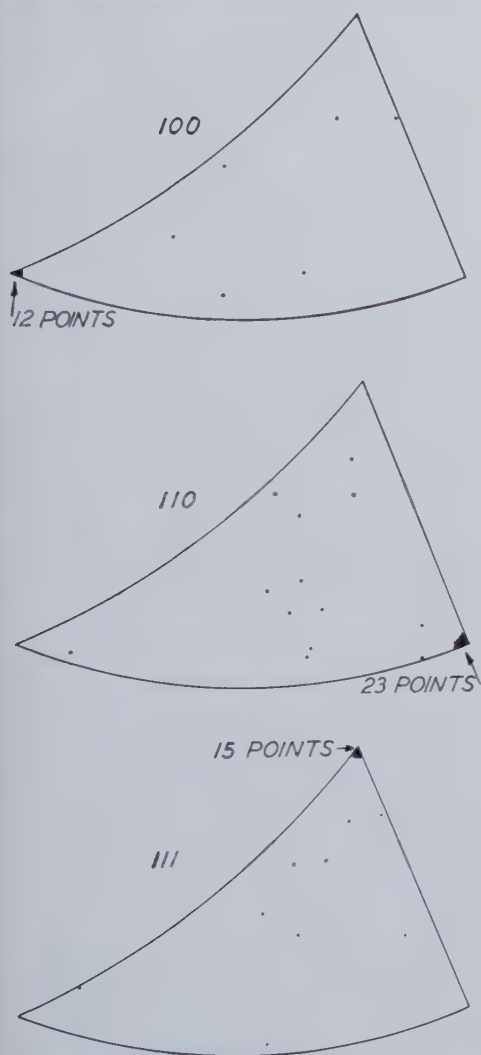


FIG. 10.—POLE FIGURES FOR BETA $\rightarrow$ GAMMA AT 400°C.

Dots are poles of diffusion layer in standard projection of core.

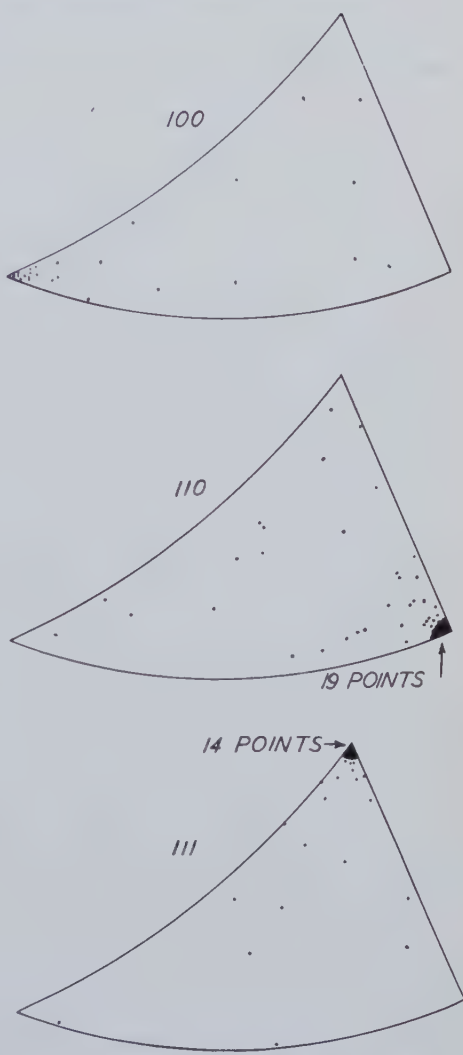


FIG. 11.—POLE FIGURES FOR BETA $\rightarrow$ GAMMA AT 500° AND 550°C.

tion is a chance process, producing, even at the saturation limit, aggregates of Zn and Cu atoms at or near the surface which approximate the beta composition; normal

analogous to ordinary precipitation resulting from temperature change. If surface adsorption is the predominating process, the nucleation is at the surface, and is

analogous to precipitation at the grain boundary upon temperature change, which is known to produce orientations identical with those within the grain, as would be

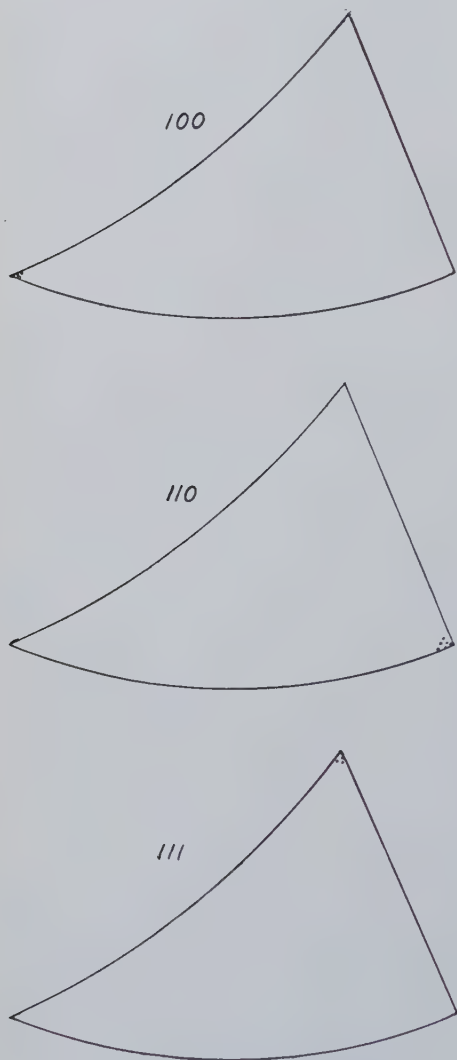


FIG. 12.—POLE FIGURES FOR GAMMA $\rightarrow$ BETA AT 400°C.
See caption of Fig. 10.

expected.^{7,15} If normal concentration fluctuations are predominating, nucleation may occur at the surface, or it may occur

below the surface; in the latter case, concentration fluctuations below but near the surface will produce concentrations that have the beta composition; ordinarily these would disappear in the next time instant, but with Zn diffusing inward, adjacent regions reach saturation and prevent their dispersion; accordingly they become stable nuclei.

Similar arguments can be advanced for the generation of alpha brass from beta by dezincing, and also for the formation of beta on alpha by the peritectic reaction. The identity in orientation relationships is, therefore, not surprising, for the argument requires that all three types of reaction consist in simple precipitation from solid solution.*

The temptation is strong to extend this principle into a general law, stating that the same two lattice types, whatever their composition, and in whatever alloy system they might occur, exhibit the same lattice orientation relationships. For example, Fe-Ni alloys exhibit the f.c.c. $\rightarrow$ b.c.c. transformation, and develop the same Kurdjumow and Sachs relationship and the neighboring Nishiyama relationship as the f.c.c. alpha and b.c.c. beta phases in the Cu-Zn system;⁸ the same relationship is found between f.c.c. gamma Fe and b.c.c. alpha Fe,¹⁷ and between f.c.c. austenite and b.c.c. ferrite in proeutectoid ferrite,⁷ in bainite¹⁴ and in tempered martensite;⁴ and it is again found to occur between the f.c.c. alpha and b.c.c. beta phases in the Cu-Sn,^{18,19} Cu-Al²¹ and Ag-Zn²⁰ systems.† In the Fe-N system, in which b.c.c. alpha Fe precipitates f.c.c. Fe₄N, the composition planes have high-order indices, but the lattice orientation relationships, which have not been completely determined, are probably very close

* The orientation relationships observed between metals and the oxides formed upon them, and among oxides formed one upon another,¹⁶ may be argued in the same way.

† When transition lattices of the martensite type occur, forming by homogeneous shear

to the Kurdjumow and Sachs relationship. In the Cu-Pd superlattice, however, where on cooling the random high-temperature f.c.c. lattice transforms to the ordered low-temperature b.c.c. lattice, the orientation relationship is quite different.² Excluding superlattices, and not attempting to include any statement concerning composition planes (thus leaving out of consideration the sequence of shearing mechanisms by which the new lattice forms from the old), the general principle is not in contradiction with information now available.*

SUMMARY

1. The orientation relationships between phase layers formed by diffusion in the Cu-Zn system have been determined.

2. The alpha phase formed on beta, and the beta phase formed on alpha, at temperatures of 400° and 700°C., take orientations clustering about the Kurdjumow and Sachs and the Nishiyama relationships.

3. The beta phase formed on gamma, and the gamma phase formed on beta, at temperatures of 400° and 550°C., take orientations with all cube axes in the two phases parallel.

4. These are the same orientations that occur when these phases form by precipitation on temperature change and when beta forms from alpha by the peritectic reaction. A mechanism is described which explains this identity in orientation relationships as originating in an identical process of nucleation.

and not by nucleation and growth, complex composition planes appear,² and these are sometimes observed even in reactions of the nucleation type,^{10,14} yet even in these the orientation relationships between the new and the old phase are the same as those occurring in ordinary precipitation.

* It will be observed that in all cases cited the two phases are adjacent in the system, and that there is no great difference in mean atomic volume. In reactions where the atomic volumes of the respective lattice types have a greater difference, it is possible that new orientations may be observed, and if this should be so, the general principle will require modification, though not the limited principle.

5. These results confirm the principle that orientation relationships obtaining between the same two phases are identical whatever the type of phase change involved. This principle probably can be generalized to refer to any two lattice types, whatever their composition; limitations on the general principle are discussed.

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DISCUSSION

(Robert Treuting presiding)

R. TREUTING,* Murray Hill, N. J.—There is one question I should like to ask Dr. Barrett. He mentioned, in reference to Fig. 5, that he found that recrystallization took place following the diffusion heat-treatment. I

* Bell Telephone Laboratories.

should be very much interested to know his thoughts as to the source of the recrystallizations, residual strains, or whatever other mechanism it may have been.

J. H. FRYE, JR.,* Bethlehem, Pa. —Dr. Barrett points out that precipitation occurs in such a way that a particular plane of the precipitated crystal forms parallel to a definite plane of the host crystal. For example, (110) of the precipitate might form parallel to (111) of the matrix. Is it possible to explain why these two planes, and not some other two, should be parallel?

C. S. BARRETT.—There seems to be no simple rule that will cover all cases. A review of

* Lehigh University.

published data for many alloy systems shows that a precipitated plate will not necessarily grow on a plane of greatest atomic density, nor even on a plane containing one of the closest packed rows of atoms, nor on the planes of cleavage, slip or twinning. It can be said, however, that in most alloys the atomic planes facing each other across the interface between the phases have very similar atom patterns and atom spacings, which would make the energy of the interface very small. Perhaps the new phase forms in such a manner as to cause the least increase in the energy of the system, or perhaps in some alloys the determining thing is the activation energy that is required to shear or distort the existing crystal into the structure of the precipitate.

Factors Affecting Rates of Work-hardening in Primary Substitutional Solid Solutions

BY J. H. FRYE, JR.,* AND C. P. SUN,* MEMBERS A.I.M.E.

(New York Meeting, February 1944)

A PRIMARY substitutional solid solution is a solution that has the same crystalline structure as the solvent metal, and in which solute atoms have replaced solvent atoms at random on the host lattice. This replacement usually results in an increase in hardness as measured by conventional penetration tests. The factors controlling this hardness increase have been investigated in some detail for copper and silver alloys.¹⁻⁵ It has been shown that at least four factors are involved: (1) concentration of solute, (2) row of the periodic table from which the solute is taken, (3) increase in lattice parameter of the solvent produced by the solute, and (4) work-hardening produced by penetration of the hardness indenter.^{2,4}

The last factor is of the utmost importance. An investigation of the available data^{2,4} leads to the conclusion that the solutes that produce large hardness increases in copper or silver do so principally because they increase the rate of work-hardening. Furthermore, it is doubtful whether any solute produces appreciable hardening in the absence of plastic deformation and hence work-hardening. Thus it is clear that an understanding of the effect of solutes on rate of work-hardening is essential to an understanding of the hardness of solid solutions.

This effect of solutes is also important in forming operations such as rolling or deep drawing. The presence of elements that confer rapid rates of work-hardening will increase power consumption and may well decrease the amount of deformation possible between anneals.

This paper is the report of an investigation of the factors that control rates of work-hardening in copper and silver solid solutions. The silver and copper alloys considered are those in which all solutes are from the B subgroups or second short period of the periodic table. Experience with hardness, with structure of alloys, and with electrical conductivity has proved that results of a fundamental nature are most likely to be obtained if alloys are made up on the basis of the positions of the constituent elements in the periodic table.

In previous work, Meyer analysis data on high-purity copper and silver solid solutions were obtained through careful measurements with fully calibrated equipment and these data were corrected to correspond to a standard grain size. From these corrected Meyer analysis data rates of work-hardening have now been calculated.

CALCULATION OF RATES OF WORK-HARDENING

The Meyer analyses, on which this study of rates of work-hardening is based, consisted in determining impression

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* Department of Metallurgical Engineering, Lehigh University, Bethlehem, Pennsylvania.

¹ References are at the end of the paper.

diameters produced by a 4-mm. ball forced into the metals or alloys under various loads. Penetration of a testing ball results in work-hardening, which

this is a measure of rate of work-hardening. For purposes of this paper rate of work-hardening will be defined as rate of increase of hardness with impression diameter.

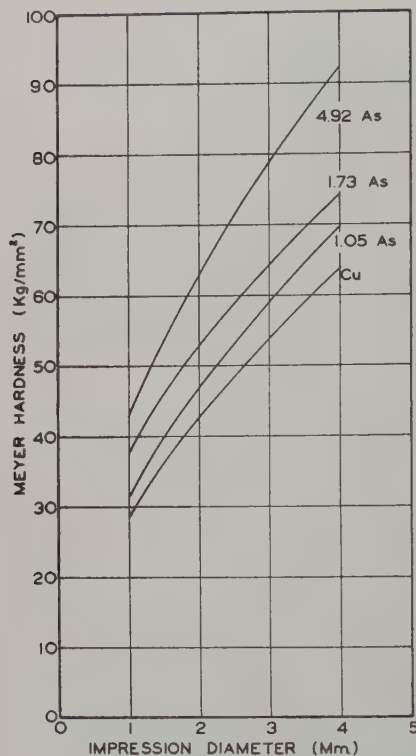


FIG. 1.—INCREASE IN HARDNESS DUE TO PLASTIC DEFORMATION PRODUCED BY PENETRATION OF A 4-MILLIMETER BALL INTO PURE COPPER AND INTO COPPER CONTAINING VARIOUS ATOMIC PERCENTAGES OF ARSENIC.

increases with increasing penetration. It is possible from such data to construct curves for hardness vs. impression diameter which are essentially stress-strain curves.⁶ Typical curves are reproduced in Fig. 1.⁴ These refer to pure copper and to copper-arsenic solid solutions of the atomic composition indicated. They cover the range from a 1 to 4-mm. impression, which is roughly the range covered in the experimental measurements. The slope of such curves at any point gives the rate of increase of hardness with impression diameter and

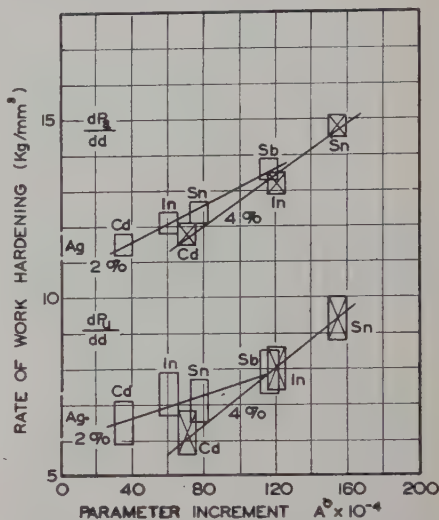


FIG. 2.—RELATION BETWEEN RATE OF WORK-HARDENING AND EXPANSION OF CRYSTAL LATTICE OF SILVER PRODUCED BY VARIOUS SOLUTES.

The two upper curves refer to a 1-mm. impression; the two lower curves to a 4-mm. impression. Plain rectangles refer to solutions containing 2 atomic per cent solute and rectangles with crosses refer to solutions containing 4 atomic per cent solute.

The Meyer⁷ hardness is defined as

$$P = 4L/\pi d^2$$

where

P = Meyer hardness,

L = load,

d = impression diameter.

It has been shown that

$$L = ad^n$$

where a and n are constants.

It follows that

$$P = 4ad^{n-2}/\pi$$

The slope of curves such as those of Fig. 1 at any given point is then given by the equation

$$dP/dd = 4a(n-2)d^{n-3}/\pi$$

From previously published Meyer analysis data,^{2,4} values of dP/dd have been calculated for 1-mm. and 4-mm. impressions. These have been designated respectively

increment for solutions in which both solute and solvent are from the same period of the periodic table. It is believed that most points are accurate within the

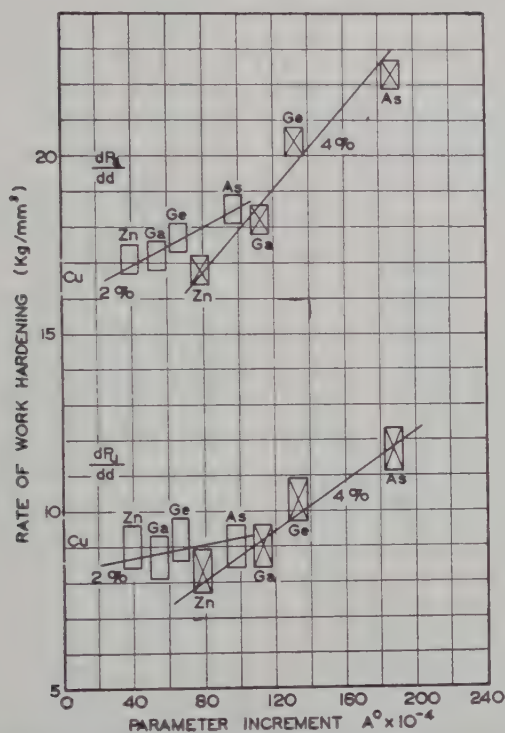


FIG. 3.—RELATION BETWEEN RATE OF WORK-HARDENING AND EXPANSION OF CRYSTAL LATTICE OF COPPER PRODUCED BY VARIOUS SOLUTES.

The two upper curves refer to a 1-mm. impression; the two lower curves to a 4-mm. impression. Plain rectangles refer to solutions containing 2 atomic per cent solute and rectangles with crosses refer to solutions containing 4 atomic per cent solute.

as dP_s/dd and dP_a/dd . The Meyer hardness corresponding to a 4-mm. impression for these alloys is roughly double that corresponding to a 1-mm. impression. Thus these values cover a considerable range of work-hardening. Values have been listed in Table 1 together with atomic percentages of solute and changes in lattice parameter of the solvent s produced by the solute.^{2,4,5}

FACTORS AFFECTING RATE OF WORK-HARDENING AND HARDNESS

In Figs. 2 and 3, rate of work-hardening has been plotted against lattice-parameter

limits indicated by the rectangles. Lattice-parameter increment is the difference between the lattice parameter of the pure metal and that of the solution. It is clear from this figure that at least three variables are involved. These are concentration of solute, plastic deformation as measured by impression size, and lattice expansion produced by the solute. When the first two variables are held constant, a linear relation within limits of experimental error is revealed between rate of work-hardening and lattice expansion. Table 1 shows, for the silver alloys at least, that

yet another variable is involved. This is the period of the periodic table from which the solute element is taken, since the relations for silver alloys shown in Fig. 2 hold only when solute and solvent are from the same period.

TABLE I.—Values for 1-mm. and 4-mm. Impressions

Alloy, Atomic Per Cent	dP_a/dd , Kg. per Cu. Mm.	dP_u/dd , Kg. per Cu. Mm.	s , Å. $\times 10^{-4}$
Pure copper	16.6	9.2	
98 Cu, 2 Zn	17.1	9.0	39
98 Cu, 2 Ga	17.2	8.7	54
98 Cu, 2 Ge	17.7	9.2	66
98 Cu, 2 As	18.5	9.0	97
96 Cu, 4 Zn	16.8	8.3	78
96 Cu, 4 Ga	18.2	9.0	112
96 Cu, 4 Ge	20.4	10.3	132
96 Cu, 4 As	22.3	11.7	187
Pure silver	11.5	6.7	
98 Ag, 2 Cd	11.5	6.5	35
98 Ag, 2 In	12.1	7.3	60
98 Ag, 2 Sn	12.4	7.1	77
98 Ag, 2 Sb	13.6	7.9	116
98 Ag, 2 Mg	11.6	6.8	17
98 Ag, 2 Al	12.2	7.7	-24
98 Ag, 2 Zn	12.2	7.5	-34
96 Ag, 4 Cd	11.8	6.2	70
96 Ag, 4 In	13.2	8.0	120
96 Ag, 4 Sn	14.8	9.4	154
96 Ag, 4 Mg	12.1	6.8	34
96 Ag, 4 Al	13.5	8.3	-48
96 Ag, 4 Zn	12.5	7.8	-68
96 Ag, 4 Au	12.3	8.1	-12

Thus rate of work-hardening depends on concentration of solute, period of the periodic table in which the solute occurs, plastic deformation, and lattice-parameter increment. When the first three of these variables are held constant, a linear relation is found between rate of work-hardening and lattice expansion.

As would be expected, the same factors also affect the hardness of these solid solutions.^{2,4} It is of particular interest that both rate of work-hardening and ultimate Meyer⁵ hardness bear a linear relation to lattice expansion. If any one of the lines of Fig. 2 or Fig. 3 is extrapolated to zero parameter increment, it intersects the axis of ordinates below the point for the pure solvent.* This is true also of the straight

lines in the previously published graph of ultimate Meyer hardness versus increase in lattice parameter (Fig. 2 of ref. 5). This implies that, while lattice expansion increases hardness and rate of work-hardening, some other factor is involved, which produces a decrease. It may be that this factor is the decrease in overlap of the electron clouds of neighboring ions that occurs when one of these solute atoms is substituted for a solvent atom. This has been discussed in some detail in an earlier paper.⁵

DISCUSSION OF RESULTS

It is widely believed that work-hardening is attributable to distortion of the crystal structure produced by plastic deformation. Such hardening would depend not only on this distortion, but also on the nature of the crystal lattice that was distorted. Thus the present work might profitably be extended to a consideration of the effect of these solutes on the properties of undeformed copper or silver and on the degree of lattice distortion produced in them by plastic deformation.

First, the elastic and plastic properties of the undeformed solvents and solid solutions might be ascertained by measurements of elastic moduli and by measurements of either the so-called critical shear stress or initial rates of flow under stress. Second, the effect of solute elements on the crystal distortion produced by plastic deformation might be ascertained through calorimetric measurements of stored energy, measurements of X-ray line intensity, and electron microscopic examinations. These data should materially enhance our understanding of hardness and rate of work-hardening in solid solutions.

SUMMARY

Earlier investigations have revealed a number of factors controlling the hardness

*Linde⁸ has shown that there is a linear relation between electrical resistance of these alloys and the square of the difference in group number of solute and solvent. It is

interesting that if the lines be extrapolated to zero difference in group numbers they do not pass through the point for the resistance of the pure solvent but below it.

of solid solutions. One of these is the rate at which the solution hardens under penetration of the hardness indenter. This factor is of extreme importance because hardness changes are partly, perhaps predominantly, the result of variations in rate of work-hardening. Factors affecting rate of work-hardening have been pointed out in this paper and have been compared with factors previously shown to affect hardness. Finally, a program of research has been suggested, which should further clarify our understanding of hardness and of rate of work-hardening in solid solutions.

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DISCUSSION

(T. A. Read presiding)

T. A. READ,* Philadelphia, Pa.—I should like to ask Dr. Frye for a clarification of the statement in the early part of the paper that "it is doubtful whether any solute produces appreciable hardening in the absence of plastic deformation and hence work-hardening . . ." It is well known, on the other hand, that the critical shear stress for a single crystal of 70-30 brass is approximately ten times that of a single crystal of copper.

J. H. FRYE, JR. (author's reply).—I am glad that Dr. Read has brought up this point, because, from his having brought it up, I judge that we did not make our meaning clear. Dr. Read is talking about the percentage increase whereas we were talking about the actual increase in hardness. What he says is correct and is of great theoretical interest.

The statement quoted by Dr. Read occurs in the introduction and was made only in an attempt to indicate the very great importance of the problem being investigated. Measured increases in indentation hardness produced by solutes are the result both of the introduction of the solute and of plastic deformation. Usually these increases are large enough to be practically useful only if there has been considerable plastic deformation. Thus the effect of a solute on rate of work-hardening is of great practical and theoretical importance.

M. GENSAMER,* Pittsburgh, Pa.—I think we should all be glad that the authors have made this important contribution to the science; but I think I ought to say also, for the record, that I am very sorry that they have chosen to discuss the problem in terms of the relatively difficult to interpret indentation hardness test. I wish that they had been able to discuss their data as stress-strain curves, and particularly true stress-strain curves. I think the advantage of this might be seen, perhaps, in a paper that Mr. Lacy and I presented last fall. Of course the objection might be raised that it is difficult frequently to get specimens big enough to make tensile tests—and there are other difficulties, particularly with soft metals—but we have been able to get around these difficulties with tensile tests by using compression tests. We have been able to get good stress-strain curves in compression using very small specimens, which are not too difficult to prepare. We have actually made compression tests, with quite good results, on specimens as small as one millimeter square and three millimeters high. I would like to see work-hardening discussed on the basis of true stress-strain tests. I hope that the authors will have a chance to further their work in that direction.

J. H. FRYE, JR.—I completely agree with Dr. Gensamer that stress-strain data are more valuable than hardness data. When this work was begun at Oxford University we wished to make tensile rather than hardness tests, but did not do so because of the expense. Larger specimens would have been required and

* Ordnance Laboratory, Frankford Arsenal.

* Carnegie Institute of Technology.

this would have greatly increased costs, since some of the elements used—silver, gold, indium—were quite expensive.

We are glad to have his valuable suggestion about the use of small specimens in a compression test and I only regret that it was impossible for him to make it at a much earlier date. Any change now would involve the virtual abandonment of a large body of consistent data. This is important because one of the chief difficulties in developing a satisfactory theory of solid solution hardness has been the impossibility of comparing data by different workers using different tests, purities, etc. It would therefore seem to me better to continue to add to this body of data than to embark now on a new type of test.

MEMBER.—Did the authors try to plot data for the same hardness number, as for the same indentation diameter? If so, what were the results?

J. H. FRYE, JR.—This is a very interesting question. In order to answer it the authors have calculated rates of work-hardening at constant hardness for the copper alloys. Rate of work-hardening has been plotted against parameter increment for different hardnesses and different solute concentrations. The curves obtained were similar to those of Fig. 3, and within limits of experimental error the authors were unable to observe any significant difference except that rate of work-hardening increased more rapidly with parameter increment than in the curves of Fig. 3.

Effect of Grain Size and Bar Diameter on Creep Rate of Copper at 200°C.

BY E. R. PARKER,* JUNIOR MEMBER A.I.M.E. AND C. F. RIISNESS*

(New York Meeting, February 1944)

THAT grain size has a great effect on the mechanical properties of metals has been recognized for a long time. Bassett and Davis¹ in 1919 did excellent work in

It is well known that at high temperatures coarse-grained test bars creep less than fine-grained bars. The relation between grain size and size of test bar,

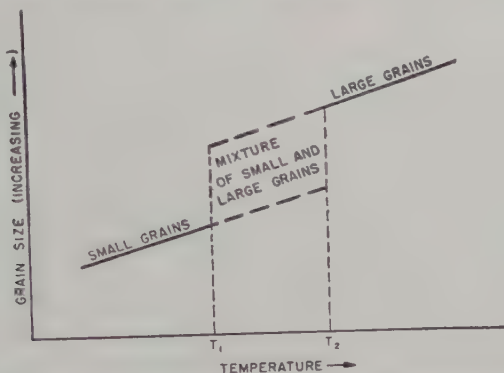


FIG. 1.—SCHEMATIC REPRESENTATION OF GRAIN-GROWTH CHARACTERISTICS OF COPPER.

determining the effect of grain size on the hardness of brass. About the same time Jeffries² and Sykes³ ascertained the effect of grain size on the strength and ductility of several metals at temperatures ranging from 80°K. to their melting points.

When creep was recognized as an important property of metals, those engaged in the study of this property tried to determine the effect of grain size⁴⁻⁹ on creep rates. Unfortunately, most of the investigations were conducted on only two grain sizes, often designated simply as "fine" and "coarse."

however, has been frequently overlooked. In his early work, Jeffries² showed that the number of grains in the cross section has a more important influence on the properties of the material than the actual grain size. More recently Hanson and Sandford¹⁰ and Pell-Walpole,¹¹ in their measurements of the creep and tensile properties of tin, tested a wide range of grain sizes and correlated the grain size with the strength. Hanson⁹ later established the relation between the number of grains in the cross section and the creep rate.

At high temperatures, generally a coarse-grained structure is considered superior in creep to a fine-grained structure, but it is evident that for a given bar size continuously increasing the grain size will

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* Research Laboratory, General Electric Co., Schenectady, N. Y.

¹ References are at the end of the paper.

not produce a corresponding continuous increase in strength. Creep tests on single crystals⁹ have shown them to be extremely weak. Consequently, when the grain

relatively fine-grained structure in a 1-in. bar.

Creep studies are complicated also by many other variables that influence the results, such as stress, temperature, strain-hardening, structural stability, alloying elements, microstructure, precipitation-hardening, grain size, test-bar size, environment. No single variable can be evaluated properly unless all other variables are controlled.

The appraisal of the grain-size effect has been further complicated because most of the studies have been made on steels having rather complicated structures. In the low-alloy, creep-resistant steels, the variables are extremely difficult to control and the measured creep rates are influenced generally by several uncontrolled factors. Structural variations such as the change in spacing of the pearlite lamellae occurring coincidentally with the change in grain size may often influence creep more than grain size. Various alloying elements also may exert an influence that overshadows the effect of grain size. In many instances the results are not clear cut, and a quantitative evaluation of the effect of grain size is impossible.

Copper was chosen for the study reported herein with the hope of avoiding many of the usual complications. The high purity (99.98 per cent Cu) and simple nature of this metal should allow the accurate evaluation of grain size and test-bar size. A testing temperature of 200°C. was chosen because a great many other high-temperature data are available for this temperature.

EXPERIMENTAL PROCEDURE

The material used for the experiments was an oxygen-free high-conductivity copper, the analysis of which is given in Table 1. Test bars of various sizes (0.505, 0.375, and 0.160-in. diameter) were machined from a 1-in. rod. The bars were

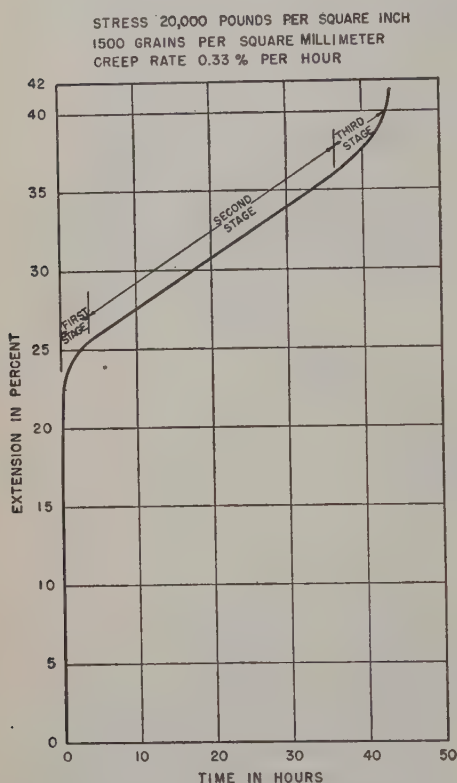


FIG. 2.—TYPICAL CREEP CURVE.

diameter approaches the bar diameter, the creep rate must increase.

From this evidence it is apparent that at high temperatures there must exist an optimum grain size; therefore a minimum creep rate. This has been suggested by Hanson,⁹ Wheeler,¹² and others. Since most creep tests have been made on bars of the same diameter, it has not generally been considered that the optimum grain size may depend on the size of the test bar. The relation between bar size and grain size becomes evident in view of the fact that a grain diameter of $\frac{1}{16}$ in. is a single crystal in a $\frac{1}{16}$ -in. bar, but constitutes a

annealed at different temperatures in purified nitrogen, to develop various grain sizes, and then subjected to creep tests at 200°C. ($\pm 1^\circ$). The temperature was

and alloys. Intermediate grain sizes were obtained by slightly cold-working the 1-in. bar before machining and annealing. This procedure shifted the small and large

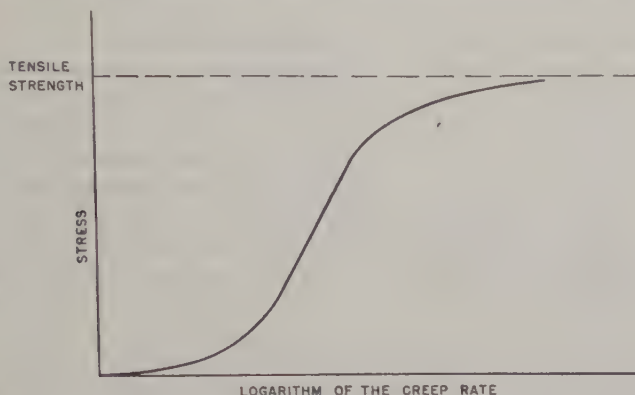


FIG. 3.—RELATION BETWEEN STRESS AND CREEP RATE.

uniform over the entire gauge length of the creep bars.

During the annealing of the bars, it was found that the grain size did not

ranges of grain size to different actual grain sizes but did not change the grain-growth characteristics previously described.

Creep rates were measured in a conventional manner by dial gauges, which indicated the relative motion of extension rods attached at each end of the gauge length. Gauge lengths of $2\frac{1}{2}$ in. were used for the 0.505 and 0.375-in. bars and 1 in. for the 0.160-in. bars.

Bars were prepared in sets of four, so that tests at four stresses could be made for each bar size and each grain size.

TABLE I.—*Analysis of the Copper*
PER CENT

Ag.....	0.0022
Fe.....	0.0015
Pb.....	0.0009
S.....	0.0023
As.....	0.0004
Ni.....	0.0008
Bi.....	0.0001
Te.....	0.0002
Se.....	0.0003
Mn.....	0.003
Sn.....	0.00005
Sb.....	0.0009
O.....	Free
Cu (bal.).....	99.988

increase continuously with increasing temperature, but increased discontinuously, as shown schematically in Fig. 1. At the temperature T_1 , the grain-size in a few regions suddenly became very large. A slight increase in temperature caused more large grains to form, but the remaining small ones did not grow appreciably. The percentage of large grains increased with temperature until at temperature T_2 all grains were coarse. Heating to higher temperatures caused slight additional grain growth. This type of grain growth has been observed in many other metals

RESULTS

A typical creep curve is shown in Fig. 2. The constant rate, shown as stage 2, was used for comparing the creep rates. Tests were made at stresses of 12,000, 15,000, 18,000 and 20,000 lb. per sq. in. on each set of bars. The relation between stress and creep rate can be expressed by a hyperbolic sine function,^{13,14} which for a certain range of stress can be approximated by an exponential function. The experimental data seem to fall within this range of stress because a straight line is formed when the stress is plotted against

the logarithm of the creep rate. At stresses near the tensile strength, deformation occurs much more rapidly than would be expected from the hyperbolic sine law.

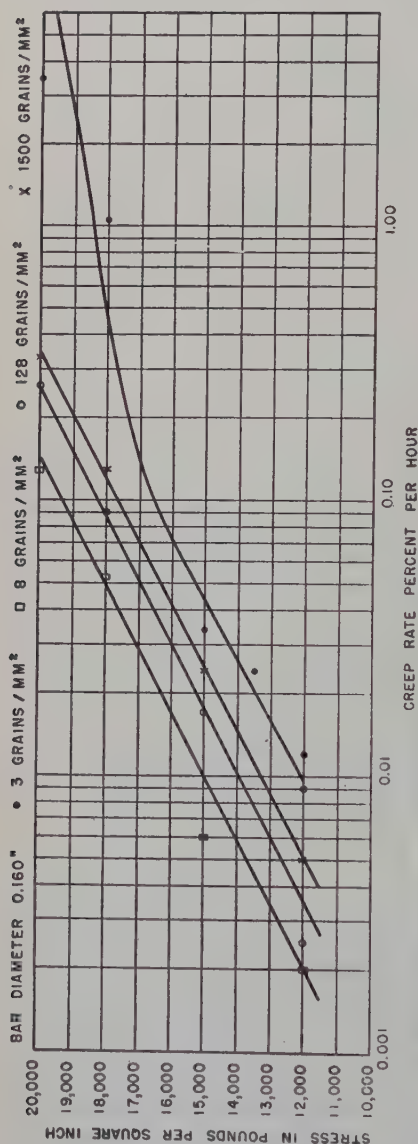


FIG. 4.—STRESS VERSUS CREEP RATE FOR 0.160-INCH DIAMETER BARS WITH VARIOUS GRAIN SIZES.

rate is shown schematically in Fig. 3. The straight part of the curve indicates the range where most of the experimental data fall. Creep rates obtained on the 0.160-in. diameter bars are shown in Fig. 4. These results clearly indicate the existence of an optimum grain size. Those on 0.375 and 0.505-in. bars did not show such a pronounced grain size effect (Figs. 5 and 6). The variation of creep rate with grain size was less than the experimental error in determining the creep rate. Grain size seemed to have very little influence on the creep rate of the large bars, whereas a pronounced effect was observed with the small bars.

This observation suggested that oxidation of the small bars was influencing the results. Such an effect had been observed for steels;¹⁵ small bars were found to be considerably weaker than large bars because of the life-shortening effect of oxidation. Consequently, it was considered advisable to determine the role of oxidation. This was done simply by cadmium-plating two sets of small bars (after heat-treating) and repeating the creep tests. The data shown in Fig. 7 indicate that oxidation played a major role in the original results. The effect of grain size could not be evaluated precisely, but the results with the cadmium-plated bars suggest that grain size has little effect on the creep rate. This is in agreement with the results on the larger bars.

An idea of the range of grain sizes studied can be obtained from Fig. 8, in which the stress required to produce a creep rate of 0.01 per cent per hour is plotted against the logarithm of the number of grains in the cross section. This stress is independent of grain size, within the limits of experimental error, for each bar size. The small bars, however, crept considerably faster than the large bars at high stresses, but at low stresses the creep rates of the small bars seem to approach those of the large bars. For

Such high loads apparently cause deformation by slip as well as by creep.

The curve obtained when the stress is plotted against the logarithm of the creep

stresses around 10,000 lb. per sq. in., neither grain size nor bar size seems to affect the creep rate of copper.

The creep rate for the two larger bar

by Hanson,⁹ who determined the room-temperature creep rate of tin specimens having 1 to 1000 grains in the cross section. Under a stress of 500 lb. per sq. in., a

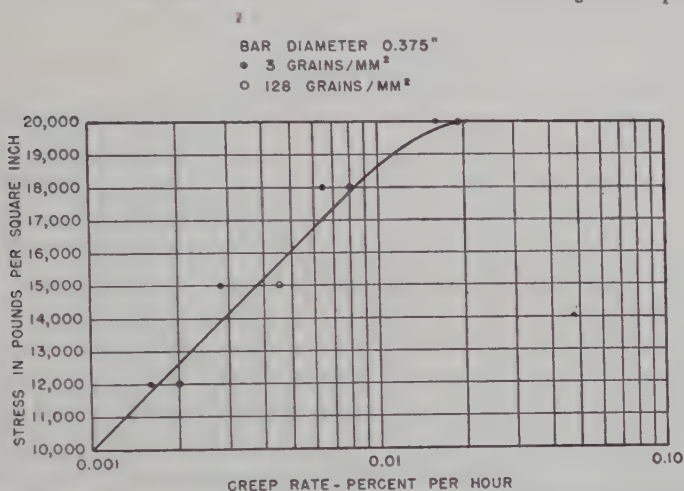


FIG. 5.—STRESS VERSUS CREEP RATE FOR 0.375-INCH DIAMETER BARS WITH VARIOUS GRAIN SIZES.

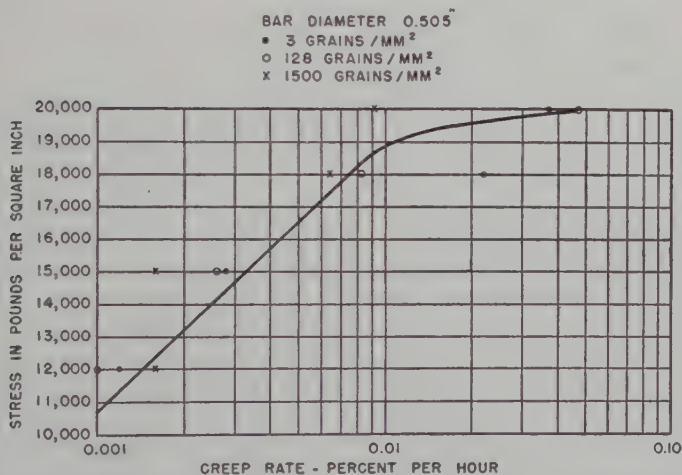


FIG. 6.—STRESS VERSUS CREEP RATE FOR 0.505-INCH DIAMETER BARS WITH VARIOUS GRAIN SIZES.

sizes was found to be independent of the number of grains in the cross section, even though the number of grains varied a thousandfold.* This was a rather surprising result in view of the results reported

single crystal elongated 24 per cent per day; a specimen with 300 grains in the cross section had the lowest creep rate, which was 0.35 per cent; and a bar with 1000 grains in the cross section had a creep rate of 2.0 per cent. Consequently it seemed advisable to consider some of

* The number of grains per square millimeter varied over a range of 3 to 1500.

the other high-temperature properties of the copper to see whether a better understanding of the results could be obtained. In previous rupture tests on this copper

grained ones, because it is acknowledged generally that the smaller grain sizes result in higher strength when tests are made below the annealing temperature.

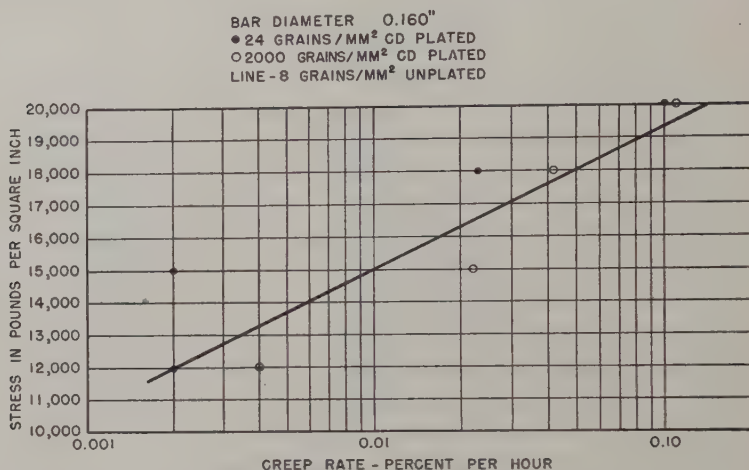


FIG. 7.—STRESS VERSUS CREEP RATE FOR 0.160-INCH DIAMETER BARS CADMIUM-PLATED TO REDUCE OXIDATION AS COMPARED WITH THE STRONGEST UNPLATED BARS.

at 150°C. the fractures were intergranular; hence it was concluded that the testing temperature of 200°C. was considerably above the "equicohesive temperature."* According to the findings of Jeffries and Archer,¹⁶ the small grain sizes should have been weaker than the larger ones.

The annealing characteristics of the copper were investigated to see whether they would aid in the understanding of the results. Pieces were reduced cold 10, 25, 50, 75, and 90 per cent. Separate pieces were heated for 20 hr. at various temperatures. The diamond pyramid hardness was measured on each piece after heating (the load used was 25 kg.). The results are shown in Fig. 9. Considerable softening does occur at 200°C. in the highly cold-worked material, but the slightly worked material does not soften appreciably in 20 hr. These results would lead one to believe that the fine-grained bars should be stronger than the coarse-

These two apparently contradictory considerations may help to explain the results. It seems possible that the testing temperature was exactly right for the strength to be independent of grain size. At other temperatures, however, the strength might be a function of grain size. Creep tests are by nature rather extensive and it has not been possible as yet to extend these studies to other temperatures.

The bar-size effect may be due in part to the weakening effect of oxidation. Whether or not this could account for the entire difference in strength is not known. Certainly the cadmium plating did not entirely prevent oxidation, and it is impossible to predict what results would be obtained if tests were conducted in a neutral or reducing atmosphere. It may safely be concluded, however, that in air a bar-size effect is to be expected.

SUMMARY

Creep tests were conducted on an oxygen-free high-conductivity copper at

* For a complete description of "equicohesive temperature," see Jeffries and Archer.¹⁶

200°C. to determine the effect of grain size on creep rate.

Grain sizes ranging from 3 to 1500 grains per square millimeter were tested in

strength, but the small bars were considerably weaker, particularly at high stresses.

The small bars seemed to be oxidized

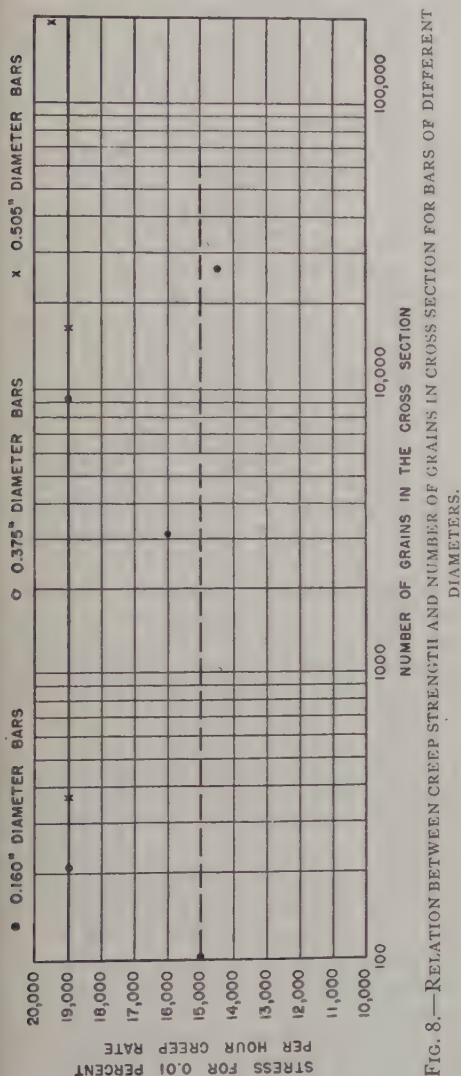


FIG. 8.—RELATION BETWEEN CREEP STRENGTH AND NUMBER OF GRAINS IN CROSS SECTION FOR BARS OF DIFFERENT DIAMETERS.

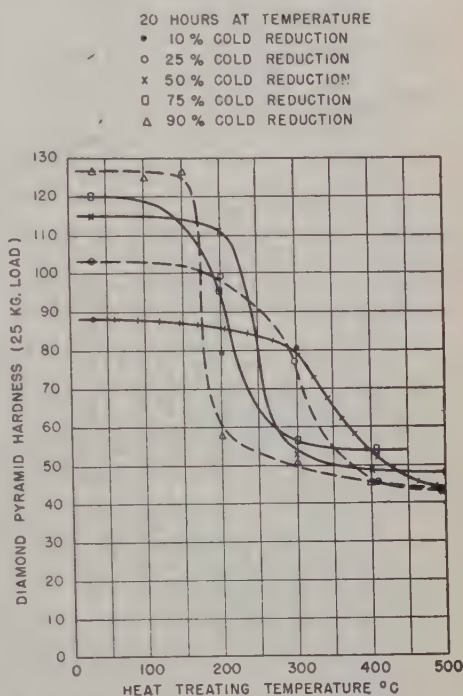


FIG. 9.—SOFTENING CURVES FOR OFHC COPPER WITH VARIOUS AMOUNTS OF COLD-WORK.

considerably, and their high ratio of surface to volume suggested that oxidation was weakening the bars. Some small bars were cadmium-plated and tested. These bars were considerably stronger than the unprotected ones. Hence it seemed that some of the difference in strength between large and small bars was due to oxidation.

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bars of 0.160, 0.375, and 0.505-in. diameter. The number of grains in the cross section of the test bars varied a thousandfold.

The creep strength was found to be independent of grain size for each bar size. The two larger sizes had equal

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DISCUSSION

(W. B. Price presiding)

A. A. SMITH, JR.,* Barber, N. J.—One thing puzzles me; that is, the effect of grain size. I think almost every investigator of the creep of metals has found that there are major effects of grain size. The work of Hanson, Chalmers and others, plus the great deal of work we have done in our laboratory on the creep of lead, has indicated that there is considerable grain-size effect.

I would like to point out to the authors that their creep data are hardly in the range

of what we would consider creep. As I recall it from looking at the curves, the lowest rates they have is something in the order of two or three thousandths of a per cent per hour. That is hardly what we would consider a creep range. When we talk about creep, we are usually interested in rates of a tenth of one per cent per thousand hours. I almost consider that their tests are slow tensile tests rather than true creep tests. I wonder if that does not have some bearing upon the fact that they show no effect of grain size.

J. S. SMART, JR.,* Barber, N. J.—In their description of the method of preparation of the samples, the authors have not mentioned the details of the processes used to produce the variations in grain size. These could have been obtained either by using very high annealing temperatures to ensure grain growth or by using light passes followed by lower annealing temperatures sufficient to produce recrystallization. If the samples were cooled rapidly, or quenched, the type of annealing treatment employed becomes of interest in creep testing because it determines whether certain impurities are present in solid solution or as precipitates. The resultant differences may very well be negligible, but until they have been evaluated it would appear desirable to provide this information to ensure the permanent value of the present work.

H. L. BURGHOFF,† Waterbury, Conn.—First, I want to recall some creep data on brass wire in the annealed condition, which was included in a paper¹ presented by our laboratory in 1942. In that paper we showed a correlation between grain size for this annealed material and creep strength, at 204°C. (400°F.) and 260°F. (500°F.). Grain sizes ranged up to 0.200-mm. diameter, and it was found that the creep strength increased as the grain size increased.

I think it would be quite interesting if the authors could give us some definite idea of the times involved in more of these tests. They show a typical creep curve for a test lasting only 50 hr., the stress being one of the highest

* American Smelting and Refining Company.

† Chase Brass and Copper Company.

¹H. L. Burghoff, A. I. Blank and S. E. Maddigan: *Trans. Amer. Soc. Test. Mat.* (1942) **42**, 668.

* American Smelting and Refining Company.

listed in the paper. Probably the tests at lower stresses were carried on for a considerably longer time. This time factor would certainly be involved in the oxidation mentioned in the paper. If there is an effect of oxidation, it is conceivable, I think, that the creep rate would vary as oxidation proceeded. I find it a little difficult to believe that oxidation at 200°C. is a very important factor if the test periods are relatively short.

Perhaps the authors have more definite ideas on the mechanism of the protection offered by the cadmium plate. Further, I wonder what actually happens to the cadmium plate. Is it in turn oxidized or is there any possibility of diffusion to the copper during the course of the test? The rate of diffusion of cadmium in copper is known to be low, but this is another factor that might alter the apparent creep strength.

E. R. PARKER and C. F. RIISNESS (authors' reply).—Mr. Smith has suggested that the stresses used were above the range usually considered in creep testing. Undoubtedly it would be advisable to continue the investigation in the lower stress range.

In answer to Mr. Burghoff's remarks, the creep curve illustrated in Fig. 2 was for a stress of 20,000 lb. per sq. in. That was a short test carried out to fracture. The tests

at the lower stresses were continued for 500 hr., or until the creep rate appeared to be constant.

As far as could be observed, there was very little oxidation of the cadmium plating on the small bars.

Mr. Smart has requested more specific information as to the processes used to produce the various grain sizes. The treatments applied to each set of bars are summarized in Table 2. The material as received was in the hot-rolled condition.

TABLE 2.—*Treatments*

Bar Diameter, In.	Cold Reduction, Per Cent	Annealing Treatment ^a	Number of Grains per Sq. Mm.
0.505	0	1 hr. 400°C. in evacuated quartz tube	128
0.505	0	1 hr. 850°C. in nitrogen	3
0.505	50	1 hr. 400°C. in nitrogen	1,500
0.375	0	1 hr. 400°C. in evacuated quartz tube	128
0.375	0	1 hr. 850°C. in nitrogen	3
0.160	0	1 hr. 400°C. in evacuated quartz tube	128
0.160	0	1 hr. 850°C. in nitrogen	3
0.160	89	1 hr. 500°C. in air	1,500
0.160	89	1 hr. 850°C. in evacuated quartz tube	8
0.160 ^b	89	1 hr. 400°C. in evacuated quartz tube	2,000
0.160 ^b	89	1 hr. 850°C. in nitrogen	24

^a All bars were furnace cooled at a rate of 100°C. per hour.

^b Bars cadmium plated after annealing.

Effect of Cooling Rate and Minor Constituents on the Rupture Properties of Copper at 200°C.

By D. L. MARTIN* AND E. R. PARKER,* JUNIOR MEMBERS A.I.M.E.

(Chicago Meeting, October 1943)

In a previous paper¹ one of the authors observed that the rate of cooling from the anneal prior to testing greatly influenced the life of copper under sustained load at 200°C. Furnace-cooled bars of oxygen-free copper (with and without silver) had a life four to twenty-five times that of the water-quenched specimens. The addition of 0.054 per cent silver to the oxygen-free copper increased the life at a stress of 20,000 lb. per sq. in. from about 2 hr. to 50 hr. Fractures in these bars were intercrystalline.

An explanation was advanced to account for the profound influence of cooling rate on the rupture properties at 200°C. The suggestion offered was that at the high annealing temperature the minor constituents are distributed at random. By water quenching, this condition is maintained at room temperature, whereas furnace cooling permits some segregation at the grain boundaries. The higher concentration of the minor constituents in the grain boundaries results in a strengthening, so that a longer life at a given stress and temperature results. Small amounts of cadmium or manganese have also been found to increase the life of copper at 200°C., and to a much greater extent than silver.²

The increase in the long-time strength of copper resulting from small additions of cadmium or silver appears to be related,

indirectly at least, to the higher softening temperatures of such alloys. The elements, such as silver or cadmium, which greatly increase the rupture life of copper also cause large increases in the softening temperature. As little as 0.05 per cent of cadmium or silver is sufficient to raise the softening temperature more than 100°. ^{3,4}

The effects of cooling rate and of minor constituents on the rupture properties are of considerable fundamental as well as practical interest; therefore a more detailed study of their nature was conducted and is reported in this paper.

EXPERIMENTAL PROCEDURE

Materials

The materials studied in this investigation may conveniently be classified in two groups: one consisting of a wide variety of commercial coppers, and the other composed of special high-purity, laboratory-prepared coppers. The commercial materials were tested to determine whether or not the effect of cooling rate occurred with all coppers, whereas the high-purity coppers were investigated in order to establish a basis for evaluating the effect of minor constituents on the rupture properties.

In Table 1 are given the analyses of the coppers tested. The samples 1 to 6 are commercial materials and were obtained for the most part from stock supplies.*

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* Research Laboratory, General Electric Co., Schenectady, N. Y.

¹ References are at the end of the paper.

* We are indebted to Mr. C. H. Hannon, Pittsfield Works, General Electric Co., for the samples Nos. 5 and 6, and to Dr. A. J. Phillips, of American Smelting and Refining Co., for Nos. 3, 4, 7, and 8.

The special laboratory coppers (Nos. 7 and 8) were prepared by the Central Laboratory of the American Smelting and Refining Co. Extreme caution was used in

in. area) for a 1-in. gauge length. The test specimens were annealed at 850°C. for one hour in a purified nitrogen atmosphere,* except the high-purity copper,

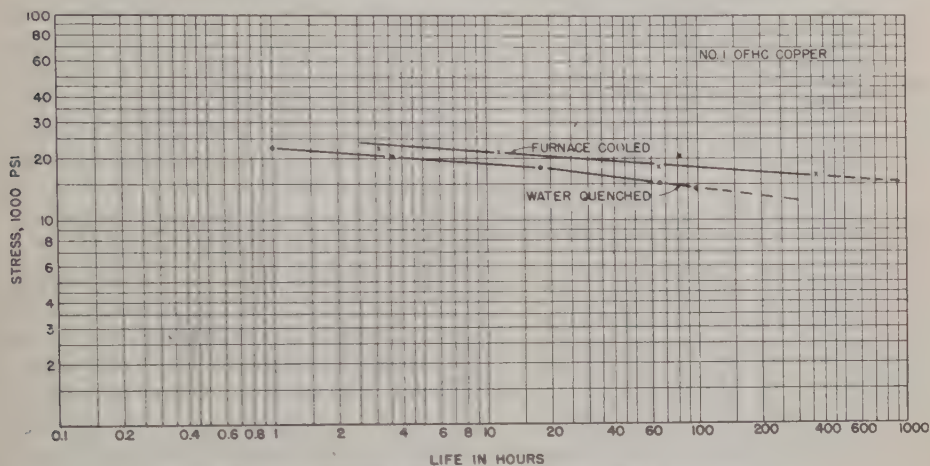


FIG. 1.—RUPTURE CURVES FOR OXYGEN-FREE COPPER.
Annealed in nitrogen at 850°C. for one hour prior to cooling.

preparing this copper in order to obtain a material 99.999 per cent pure or better.⁵ The synthetic wirebar material (No. 7) was made by adding the impurities commonly found in commercial wirebar to the molten high-purity copper under conditions to give an oxygen-free copper. We were very fortunate to obtain these special coppers for our investigation, as it was necessary to test a copper essentially free from all impurities in order to evaluate properly the effect of minor constituents on the rupture properties.

Method of Testing

All the coppers were tested in air at 200°C. in a vertical rupture furnace by subjecting test bars to various constant loads and measuring the time required for fracture. Elongation and reduction of area values were determined after fracture. The test specimens were machined from cold-swaged 0.25-in. diameter rods and were 2 in. long with quarter-twenty threads at each end. The diameter of the center portion of the bar was 0.159 in. (0.020 sq.

which was heated in vacuum (3×10^{-6} mm. pressure). Half of the bars were cooled in the furnace at approximately 100°C. per hour and half were water-quenched.

The heat-treated bars were tested by suspending them with long extension rods in the hot zone of the rupture furnace. The loads were applied through simple levers. The temperature was automatically controlled within 1° centigrade and the temperature gradient in the furnace was less than 1° in 4 in. The life of each bar was measured with an hour meter, which was automatically tripped off when the bar broke.

RESULTS

In Figs. 1 to 8 are given the rupture curves of the coppers listed in Table 1. These are plotted on log-log paper, life

* The nitrogen was passed over copper chips at 800°C. several times, each pass being followed by a P_2O_5 drying treatment. Copper oxide (Cu_2O) decomposed when heated in this gas.

TABLE 1.—*Analyses of the Materials*
PER CENT

Material	No.	Ag	Fe	Pb	S	As	Ni	Bi	Te	Se	Mn	Sn	Sb	O	Cu (Bal.)
Commercial oxygen-free copper ^a	1	0.0022	0.0015	0.0009	0.0023	0.0004	0.0008	0.0001	0.0002	0.0003	0.0003	0.00005	0.0009	Free	99.983
Commercial silver-bearing oxygen-free copper ^a	2	0.054	0.0005	0.0003			0.0004	0.00005				0.0002	0.0004	Free	99.944
Tough-pitch oxygen (low impurity) ^{b,c}	3	0.0018	0.0007	0.0004	0.0013 ^d	0.0003	0.0002	<0.00001	0.0001			NI	0.0002	0.035 ^d	99.961
Tough-pitch copper (high impurity) ^{b,c}	4	0.0018	0.0006	0.0010	0.0013 ^d	0.0004	0.0025	0.0001	<0.0001			0.0090	0.0007	0.035 ^d	99.947
Silver-bearing tough-pitch copper ^a	5	0.029	0.0012	0.0010	0.0013 ^d	0.0007	0.0032	NI	0.0001	0.0003		0.0001	0.0007	0.035 ^d	99.920
Commercial casted, oxygen-free copper ^a	6	0.008	0.0009	0.0000	0.0005	0.0005			0.0001	0.0005			0.0006	Free	99.995
Synthetic wirebar copper, oxygen-free ^a	7	0.0017	0.0023	0.001	0.002	0.001	0.001	0.0005		0.0005			0.002	Free	99.987
Spectrographically pure oxygen-free copper ^{a,e}	8				High-purity	A. S. and R.			Copper						
														99.999 + per cent Cu	

^a As determined by the analytical section, Pittsfield Works, General Electric Co.^b As determined by the American Smelting and Refining Co.^c Materials obtained through the courtesy of Dr. A. J. Phillips, of American Smelting and Refining Co.^d Estimated value.^e The casted copper contained nonmetallic impurities.

in hours being plotted against the stress in pounds per square inch.

Of particular interest is the shorter life of the water-quenched specimens. For example, in Fig. 1 the water-quenched material has a life of 18 hr. at 18,000 lb. per sq. in. compared with 100 hr. for furnace-cooled bars at the same stress. Surprisingly, the effect of cooling rate is very pronounced even in the case of the spectrographically pure copper (Fig. 8).

The ductility usually is greatly reduced by the water-quenching treatment. The results plotted in Figs. 9 and 10 for copper No. 7 are typical of all the materials tested.

A summary of the rupture-test results is presented in Table 2, where the values for life, elongation, and reduction of area are listed for various stresses. In brief, the effect of water quenching from the annealing temperature is to decrease the rupture life and reduce the ductility of the copper. Spectrographically pure copper (99.999+ per cent) responds to heat-treatment in the same manner as the impure coppers.

The nature of the fracture is in general transcrystalline for short-time tests and intercrystalline for long-time rupture tests. Typical examples of these two types of failures are shown in Fig. 11.*

DISCUSSION OF RESULTS

Influence of Minor Constituents

The effect of minor constituents on the rupture properties is difficult to evaluate exactly because the role played by other variables such as grain size is not completely understood; nevertheless, a few qualitative statements may be made:

1. A comparison of the data for coppers 7 and 8 in Table 2 shows that the addition of as little as 0.012 per cent of minor metallic constituents to high-purity copper is sufficient to increase the life from 9 hr.

* A more detailed discussion of high-temperature failures in metals is given in a paper by E. R. Parker.⁶

TABLE 2.—Comparison of the 200°C. Rupture Properties of the Coppers

Treat- ment	24,000 Lb. per Sq. In.			22,500 Lb. per Sq. In.			20,000 Lb. per Sq. In.			18,000 Lb. per Sq. In.			Material
	Hr.	Elonga- tion, per Cent in 1 In.	Reduc- tion of Area, Per Cent	Hr.	Elonga- tion, per Cent in 1 In.	Reduc- tion of Area, Per Cent	Hr.	Elonga- tion, per Cent in 1 In.	Reduc- tion of Area, Per Cent	Hr.	Elonga- tion, per Cent in 1 In.	Reduc- tion of Area, Per Cent	
1 F. C. W. Q.	2.5 0.7	26 27	43 38	5.5 1.0	24 25	40 36	28 5	21 21	37 28	100 18	19 18	34 23	Commercial oxygen-free
2 F. C. W. Q.	2.5 0.5	33 35	48 53	11 2.5	29 30	44 44	380 50	22 23	36 32	>1000 600	<20 18	34 24	Commercial silver-bearing oxygen-free
3 F. C. W. Q.	0.2 0.2	75 58	71 68	1.0 1.0	56 43	70 49	10 3	38 36	43 39	30 10	31 29	34 31	Tough-pitch (low impurity)
4 F. C. W. Q.	0.5 0.2	53 46	54 47	2.5 0.6	43 39	47 41	10 3	36 30	39 33	40 15	30 24	31 27	Tough-pitch (high impurity)
5 F. C. W. Q.	15 4.5	56 49	69 57	80 30	54 45	63 43	>1000 300	<50 40	<55 30	>1000 >1000			Silver-bearing tough-pitch
6 F. C. W. Q.	0.3 0.3	32 28	47 47	0.8 0.8	27 23	37 36	2 2	22 20	20 27	5 4	19 17	23 22	Commercial coalesced oxygen-free
7 F. C. W. Q.	7.0 0.3	35 30	48	16 0.6	30 25	40	60 2.5	25 21	30	220 8	21 17	24 20	Synthetic copper oxygen-free
8 F. C. W. Q.	0.4 0.1	19	42 63	0.9 0.2	18	38 50	2.8 0.6	16	33 35	9 1.7	14	29 26	High-purity, oxygen-free

to 220 hr. for furnace-cooled material stressed at 18,000 lb. per sq. in., or more than a twenty-fold increase.

2. Nonmetallic inclusions such as oxides appear to reduce the resistance to fracture.

coalesced copper may account for the low properties of this material, although the high purity of the material is also a factor.

Smart and Smith⁴ have shown that in oxygen-bearing copper some metallic im-

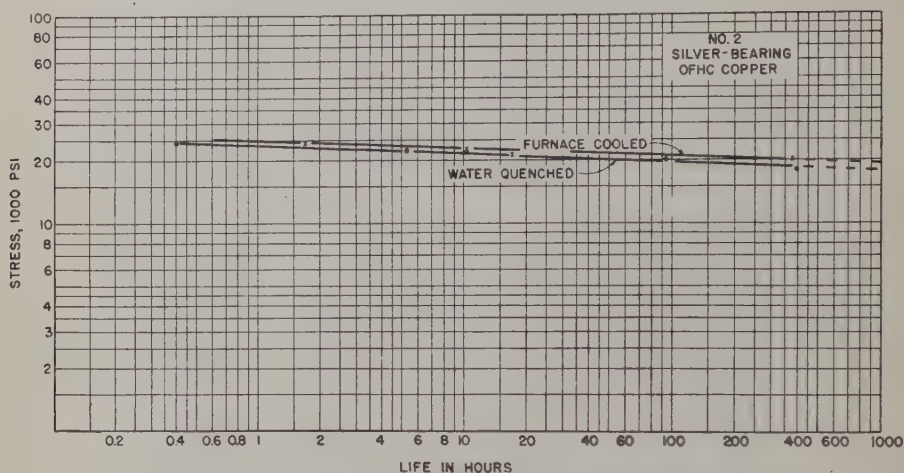


FIG. 2.—RUPTURE CURVES FOR SILVER-BEARING OXYGEN-FREE COPPER.
Annealed in nitrogen at 850°C. for one hour prior to cooling.

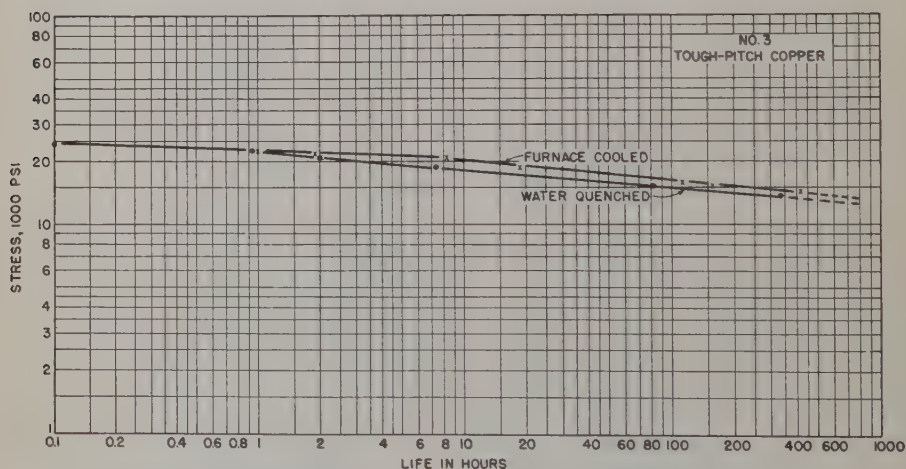
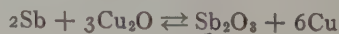


FIG. 3.—RUPTURE CURVES FOR LOW-IMPURITY TOUGH-PITCH COPPER.
Annealed in nitrogen at 850°C. for one hour prior to cooling.

The tough-pitch coppers (No. 3 and 4) are comparable in analyses to the synthetic wirebar copper (No. 7) except for oxygen content; nevertheless a 1 to 5 ratio exists for life at a given stress. Similarly, the presence of nonmetallic impurities in the

purities tend to exist in solid solution when quenched from a high temperature and as oxides when slowly cooled. The reaction may be written, for antimony, as follows:



At high temperatures, above 400° to 600°C. , the equilibrium is shifted so that it favors the formation of $\text{Sb} + \text{Cu}_2\text{O}$, and most of the antimony is dissolved in

in furnace-cooled copper containing oxygen the elements will be present as oxides.

Therefore, the role of oxygen in reducing the life might also be one of purification

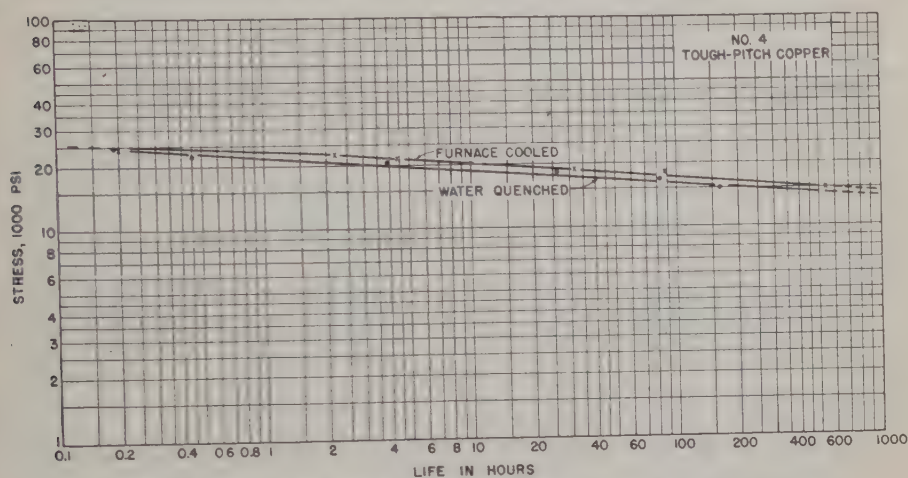


FIG. 4.—RUPTURE CURVES FOR HIGH-IMPURITY TOUGH-PITCH COPPER. Annealed in nitrogen at 850°C. for one hour prior to cooling.

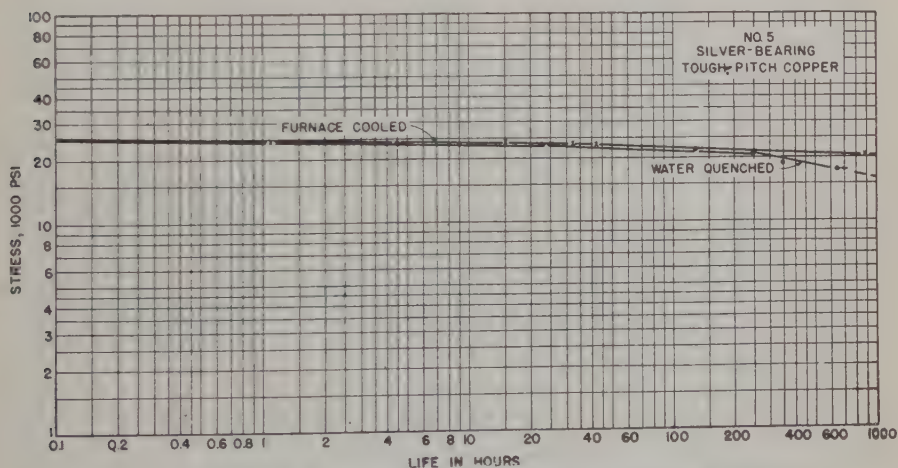


FIG. 5.—RUPTURE CURVES FOR SILVER-BEARING TOUGH-PITCH COPPER. Annealed in nitrogen at 850°C. for one hour prior to cooling.

the copper. Equilibrium conditions below 400°C. favor the formation of antimony oxide. In oxygen-bearing copper water-quenched from above 600°C. the minor constituents, such as antimony, will generally be dissolved in the metal; whereas

of the copper matrix. In a furnace-cooled tough-pitch copper some impurities (those whose oxides are more stable than cuprous oxide at low temperatures) would exist primarily as oxides; therefore the matrix would be a purer copper of lower resistance

to rupture than copper containing dissolved impurities (that is, it would be similar to copper No. 8 compared with No. 7). According to this explanation, the

tude for oxygen-free or oxygen-bearing copper of similar analyses, since the minor constituents are dissolved in the matrix in both coppers. This appears to be true,

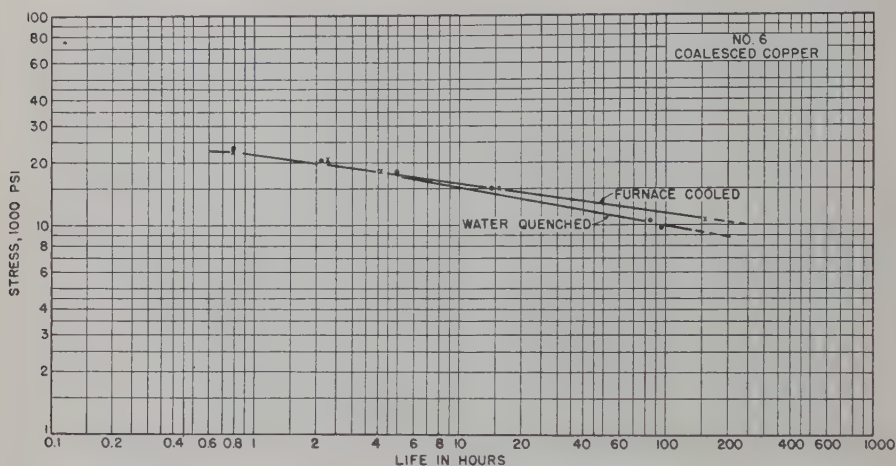


FIG. 6.—RUPTURE CURVES FOR COALESCECED COPPER.
Annealed in nitrogen at 850°C. for one hour prior to cooling.

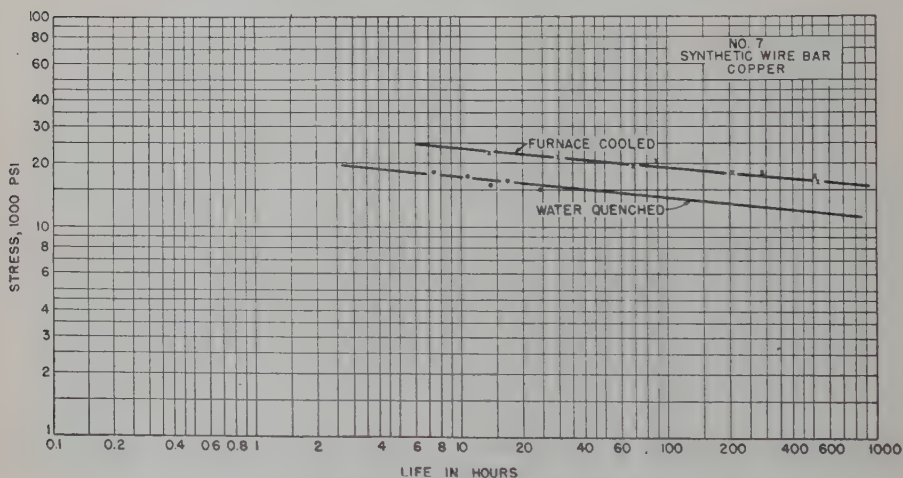


FIG. 7.—RUPTURE CURVES FOR SYNTHETIC WIREBAR COPPER.
Annealed in evacuated quartz tubes at 850°C. prior to cooling.

furnace-cooled bars of oxygen-bearing coppers should be intermediate in life between high-purity copper and an oxygen-free copper of the same composition, whereas in the water-quenched samples the life should be of the same order of magni-

for the furnace-cooled tough-pitch coppers (Nos. 3 and 4) are intermediate in life between the synthetic wirebar material, No. 8 (i.e., an oxygen-free material of comparable composition to the tough-pitch coppers), and the high-purity copper.

The water-quenched tough-pitch coppers are much the same as the synthetic wirebar copper in the same condition.

TABLE 3.—*Softening Temperature and Grain Size of the Coppers*

Coppers	Softening, Deg. C.	Grain Size, Average Diameter, Mm.
No. 7, synthetic wirebar.....	330 ^a	0.145-0.400
No. 4, tough-pitch.....	280	0.100-0.145
No. 2, OFHC + Ag.....	275	0.575
No. 3, tough-pitch.....	250	0.100-0.200
No. 6, coalesced.....	240	Duplex
No. 8, high-purity.....	200	0.575
No. 1, OFHC.....	^b	0.575-0.650
No. 5, tough-pitch + Ag.....	^b	0.070-0.100

^a The softening temperature was determined on 50 per cent cold-rolled material using the half-hard method of Smart, Smith, and Phillips.¹

^b Softening temperatures were not determined.

There are at least two opposing factors operating in furnace-cooled, oxygen-bearing copper: (1) Furnace cooling is respon-

sible for the oxygen-bearing coppers than for oxygen-free copper. Therefore, it seems likely that oxidation of the impurities

TABLE 4.—*Effects of Grain Size and Annealing Temperature on Life of High-purity Copper at Various Stresses*

Stress Lb. per Sq. in.	850°C. Anneal		500°C. Anneal		850°C. + 500°C. Anneal	
	Hours		Hours		Hours	
	F. C.	W. Q.	F. C.	W. Q.	F. C.	W. Q.
18,000	9	1.7	46	42	20	
16,500	18	3.5	81	74	30	18
Grain size..	0.575 mm.		0.050 to 0.145		0.575	

during cooling weakens the material, thus partially overcoming the strengthening effect of the furnace cooling.

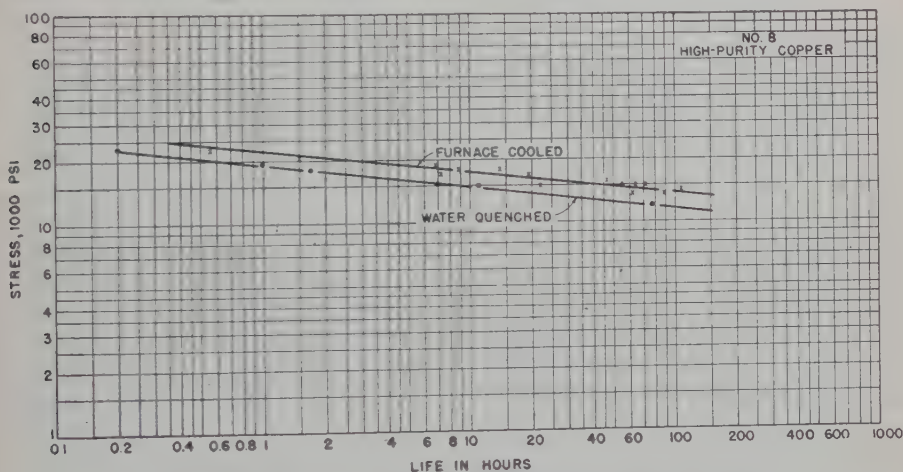


FIG. 8.—RUPTURE CURVES FOR HIGH-PURITY COPPER. Annealed in evacuated quartz tubes at 850°C. prior to cooling.

sible for a decrease in life because of the purification of the copper matrix by the oxidation of the impurities; (2) furnace cooling is also responsible for an increase in life as shown in Fig. 8. A possible explanation for this increased life is offered later in the text. The difference in life between furnace-cooled and water-quenched

3. The coppers with high softening temperatures tend to have greater resistance to rupture at 200°C., although softening temperature is definitely not the only factor involved. In Table 3 are listed the softening temperatures of most of the coppers tested. It should be noted that the materials with the highest softening

temperatures (No. 2 and 7) last longer at a given stress than the purer coppers (No. 6 and 8), which soften at lower temperatures.

4. Grain size is an important variable.

grains (Table 4). Likewise, No. 7 has smaller grains than the high-purity copper, No. 8; consequently the greater resistance to rupture possessed by copper 7 probably

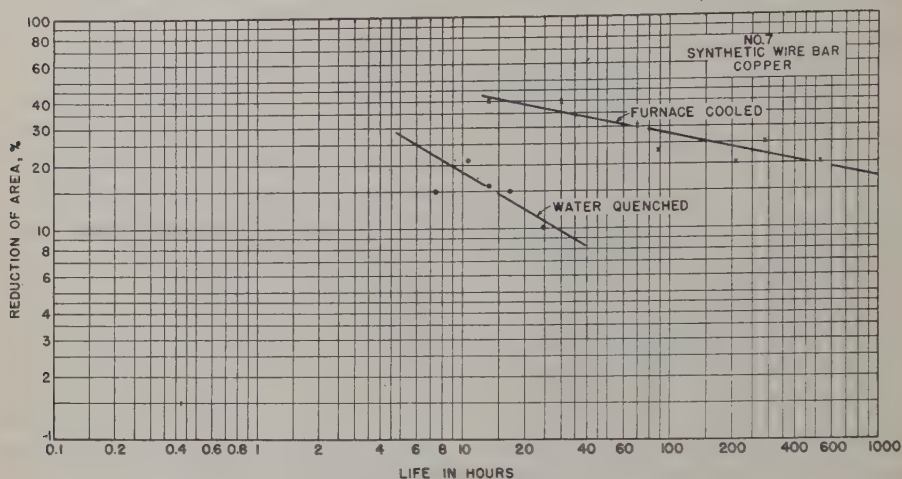


FIG. 9.—REDUCTION OF AREA VS. LIFE, SYNTHETIC WIREBAR COPPER.
Values determined on fractured bars.

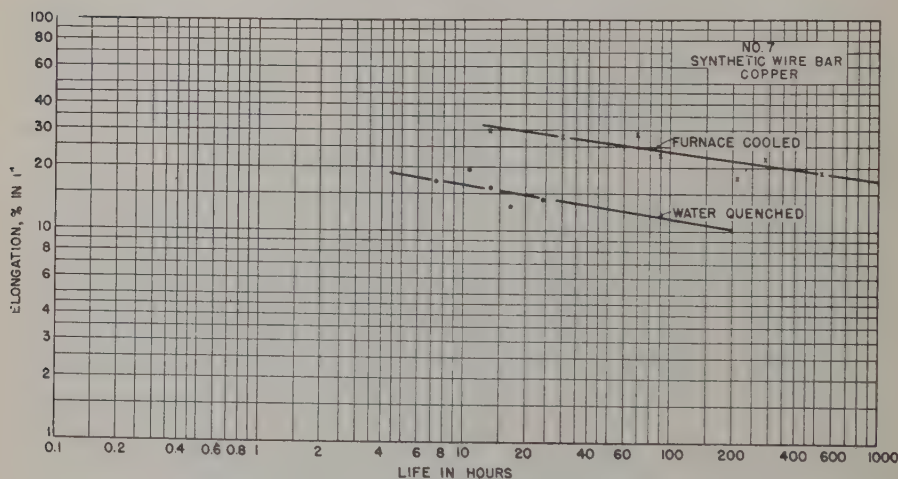


FIG. 10.—ELONGATION VS. LIFE, SYNTHETIC WIREBAR COPPER.
Values determined on fractured bars.

High-purity copper annealed at 500°C. (0.050 to 0.145-mm. grains) before testing had a longer life (Table 4) than when annealed at 850°C. (0.575-mm. grains).

It is quite possible that the greater strength of the silver-bearing tough-pitch copper (No. 5) is due in part to its finer

is not due entirely to minor constituents, per se.

Influence of Cooling Rate

1. The effect of cooling rate on the rupture properties of copper, as indicated in Figs. 1 to 8, is surprising, especially since

the spectrographically pure copper responds similarly to the impure coppers.

It is natural to suspect that the high-purity copper contains some impurity not detected spectrographically, such as carbon or gases, to which the observed effect may be attributed, so it is pertinent to review the history of this material and consider the possibility that such impurities may be present.

The possibility of dissolved gases seems remote, since the high-purity copper was melted under nitrogen.⁵ During the processing, the bar was hot-rolled in air but exposed at a high temperature only for a few minutes. The outside portion of the bars was always removed during the machining of the specimens. The annealing treatments prior to testing were carried out in evacuated quartz tubes in order to reduce gaseous contamination to a minimum.

There is, of course, the possibility of carbon being present, since the copper was melted in high-purity graphite; however, the electrical conductivity of the copper is very high (102.3) and is not changed to any appreciable extent by saturating with oxygen⁶ (which would oxidize the carbon), indicating that at most there is only an extremely small amount of carbon in solution. In view of the careful preparation and analysis (including the conductivity tests) of this material by Smart, Smith, and Phillips, it seems likely that copper No. 8 is 99.999+ per cent pure.

Assuming that the high-purity copper is truly pure, some factor other than "impurities" must account for the effect of cooling rate on the rupture strength. But what other factors can be responsible for such an effect in a pure metal, which does not undergo an allotropic transformation? The answer to this question must, it seems, be related to the degree of perfection of the crystal lattice. At high temperatures the lattice presumably is less perfect because of local thermal fluctuations and so contains imperfections in the atomic

arrangement. In the simplest case the imperfections consist of vacant lattice sites. At low temperatures the fluctuations are smaller, and the lattice is more nearly

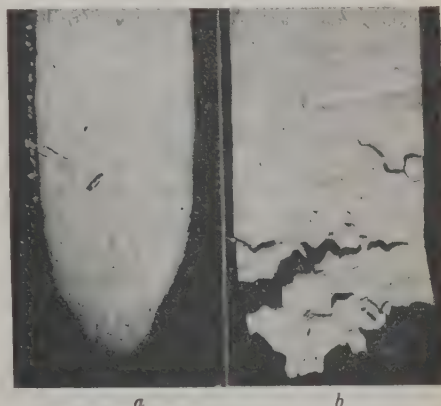


FIG. 11.—HIGH-TEMPERATURE FRACTURES IN COPPER.

a. Short-time transcrystalline fracture.
b. Long-time intercrystalline fracture.

perfect. Slow cooling from a high temperature allows the atoms to arrange themselves in nearly equilibrium locations, while rapid cooling may tend to "trap" an abnormally high number of imperfections in the lattice. Such imperfections are responsible for the weakness of metal crystals,⁷ and could be especially effective if they were concentrated at the crystal boundaries (the fractures considered in this discussion are of the intercrystalline type). The defects in the crystal boundaries or lattice act as stress raisers and cause plastic flow to start at unusually low loads. Consequently, such imperfections weaken the material.* The water-quenched bars should be weaker than those that were furnace-cooled because more imperfections are present in the rapidly cooled material.

The foregoing discussion also applies to the impure coppers, but the results are modified slightly by the minor constituents, especially in the presence of oxygen.

*For a more detailed discussion of this subject the reader is referred to references 6, 7, 8, and 9.

2. If water quenching from a high temperature results in the retention of an abnormally high number of lattice imperfections, then other metals, such as silver, should show differences in properties with cooling rate. Preliminary tests on silver did show a definite effect of cooling rate on the rupture life at 150°C.*

3. Water-quenching from 500°C. should have less effect on the life than quenching from 850°C. because fewer imperfections would be present at 500°C., so that a smaller number would be "trapped" by rapid cooling. Tests were conducted to substantiate this proposal, and the results are given in Table 4. Variations in cooling rate from low annealing temperatures cause only slight differences in rupture properties.

Influence of Lattice Imperfections on Various Properties

1. Tensile tests at room temperature† and short-time tests at 200°C. revealed little or no difference between the strength of water-quenched and furnace-cooled bars (fractures in these tests are transcrystalline). Apparently the strength of the crystalline material was not affected by the cooling rate. Long-time tests at 200°C. show big differences in life between furnace-cooled and water-quenched bars (the fractures in these tests are intercrystalline). It seems that the rapid cooling has a large effect on the strength of the crystal boundaries and relatively

* Material tested was Handy and Harman spectrographically pure silver (99.995+ per cent). For a stress of 12,000 lb. per sq. in. the life was 143 hr. for the water-quenched silver compared with 273 hr. for the furnace-cooled material.

† The room-temperature tensile results on bars heated to 850°C. in nitrogen are:

Bars	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent in 1 In.	Reduction of Area, Per Cent
Water-quenched.....	39,750	43	75
Furnace-cooled.....	39,500	44	70

little effect on the strength of the crystals, indicating that the imperfections are concentrated at crystal boundaries.

2. In addition to the rupture test at high temperatures, there should be other tests that are sensitive to the structural changes accompanying cooling. In general such tests as rupture, creep, or fatigue, which involve long periods of time, should, it seems, reveal differences in properties of a copper subjected to various cooling rates; that is, the furnace-cooled material should have properties different from those of the water-quenched copper.

Creep tests were made at 200°C. on furnace-cooled and water-quenched specimens. A great difference was observed in the creep characteristics; one of the most outstanding examples of the effect of cooling rate on creep is shown in Fig. 12. As expected, the water-quenched bar had a much greater creep rate than the furnace-cooled bar.

3. Internal friction is also a structure-sensitive property greatly influenced by lattice imperfections. Read¹⁰ has shown that the damping increases with the number of free dislocations present. Consequently, water-quenched samples might be expected to have a higher damping coefficient than furnace-cooled bars. Damping measurements were made on coppers 7 and 8 in a manner similar to that used by Read.¹⁰ The results are listed in Table 5. The data on copper No. 7 are in accord with the theory. The results on No. 8, however, are questionable because this copper was very sensitive to handling. In one instance the damping changed by a factor of five because of excessive handling during treatment and testing.* The damping of copper No. 7 did not change under the same conditions of handling. The samples were handled with extreme care for the final damping tests: but caution should be used in drawing conclusions

* Read has shown similar effects in his work on deformation vs. internal friction.¹⁰

from measurements of such a sensitive property. The data for copper No. 7 at least seems to substantiate the proposed existence of more imperfections in the water-quenched bars.

TABLE 5.—*Internal Friction* of Coppers 7 and 8 after Various Treatments*

Copper	Logarithmic Decrement, Per Cent		
	Initial State Cold-worked	Furnace-cooled from 850°C.	Water-quenched from 850°C.
No. 7, synthetic wirebar.....	0.11	0.20	0.30
No. 8, high-purity..	0.06	0.30	0.30

* Determined by Dr. R. O. Fehr and Miss Hazel Morris, General Engineering Laboratory, General Electric Company.

4. From Read's work on damping it is known that cold plastic deformation produces imperfections.¹⁰ Therefore, cold-deforming a furnace-cooled bar should introduce more imperfections* (or dislocations), and thus make the copper weaker. Examination of Table 6 will show that this is true for small degrees of prior cold-work (items 5 to 8 in the table) but that beyond a certain degree of cold-work the life increases (item 1 to 4). In other words, a slight degree of cold-work will shorten the life of a furnace-cooled sample (i.e., the metal "strain-weakens" instead of strain-hardens) presumably by introducing additional dislocations;† in a like manner water quenching from a high temperature apparently results in the retention of imperfections which weaken the metal.

The changing effect of cold-work on the life of copper in a rupture test can be explained by the dislocation theory of slip as derived by Taylor, Orowan, and others.⁷⁻¹⁰ The slip of metals occurs by

motion of imperfections through the crystal lattice, while work-hardening results from the stoppage of dislocations; that is, if the imperfections are free to move the metal will creep easily, but if the dislocations are locked together and unable to move, the metal will have a greater resistance to slip. When a slowly cooled copper bar (having a minimum number of dislocations) is plastically deformed a small amount, only a relatively few additional dislocations are produced, many of which are free to move and thus produce slip at lower stresses than in the furnace-cooled material. Larger amounts of deformation (as by reducing 10 per cent in area by swaging) produce greater numbers of imperfections but in this case they are apparently locked together and unable to move, resulting in a stronger material.

TABLE 6.—*Effect of Prior Cold Deformation on Rupture Life of High-purity Copper at 200°C.*

Treatment (all bars annealed at 850°C.)	Stress, Lb. per Sq. In.	Life, Hr.	Elongation, ^a Per Cent in 1 In.	Reduction of Area, ^a Per Cent
1. Furnace-cooled 100°C. per hour.....	18,000	9	14	29
2. Water-quenched.....	18,000	1.7		26
3. Furnace-cooled, swaged, 10 per cent reduction of area.....	18,000	69	10	15
4. Furnace-cooled, swaged, 10 per cent reduction of area.....	17,250	87	6	15
5. Furnace-cooled 100°C. per hour.....	15,750	46	14	30
6. Furnace-cooled 100°C. per hour, +3.5 per cent elongation.	15,750	14	11	25
7. Furnace-cooled 25°C. per hour.	15,750	74	13	35
8. Furnace-cooled 25°C. per hour. bar slightly bent.....	15,750	29	13	35

^a Measured on the ruptured bar.

* The term "imperfections" is used in the same sense as dislocations in the text. Other types of imperfections are known to exist in crystals; e.g., mosaic structures.

† The effect of cold-work on the life of a furnace-cooled sample was determined only for the high-purity copper.

In addition to the data reported in this paper, other evidence¹⁰⁻¹³ has been published which indicates that cold plastic deformation does not always result in a

material with increased resistance to further deformation, but may, initially at least, produce a condition more favorable for slip.

dislocations move under the influence of a cyclic stress and thereby dissipate the vibrational energy as internal friction loss. In the early stages of deformation few

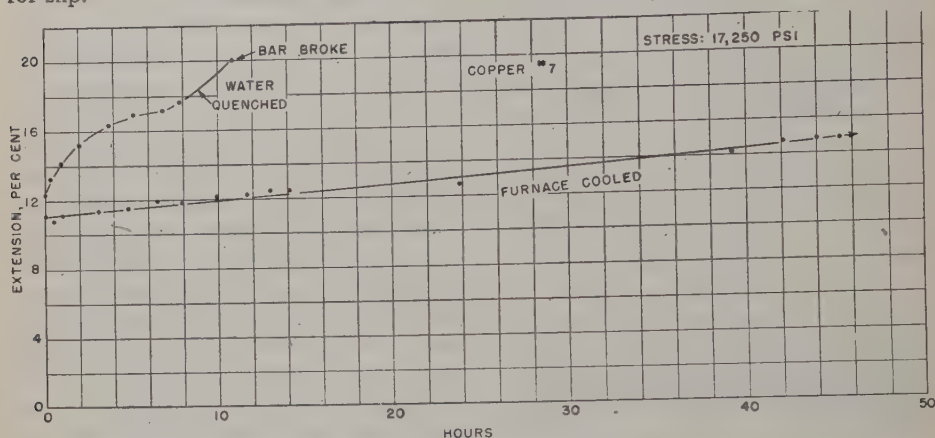


FIG. 12.—CREEP CURVES FOR COPPER NO. 7 TESTED AT 200°C. IN VARIOUS CONDITIONS.

Read, for example, has shown* that internal friction is affected differently by small and large amounts of cold-work.¹⁰

dislocations are formed, and these are free to move; therefore, increasing cold-work results in increasing damping. After some deformation, the maximum number of free dislocations is reached. Additional deformation generates more dislocations, which unite with free dislocations and become "locked," so that neither is free to move or dissipate energy. The internal friction then decreases with increasing amounts of cold-work.

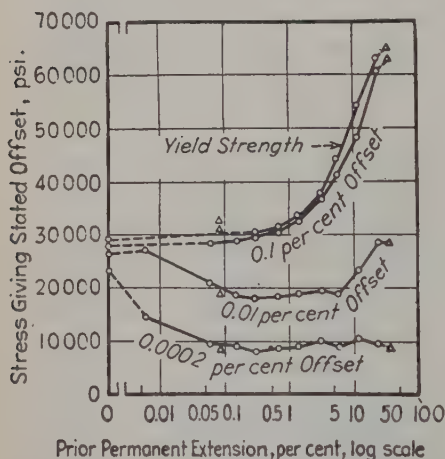


FIG. 13.—EFFECT OF PRIOR PLASTIC EXTENSION ON STRESS CORRESPONDING TO VARIOUS AMOUNTS OF OFFSET FROM PROPORTIONALITY. (C. S. Smith.¹¹)

Initially the damping is increased by deformation, but decreased after a certain critical amount of cold-work. The explanation offered by Read is that the free

C. S. Smith gives additional evidence of "strain-weakening," or the decrease in strength by plastic deformation.^{11,12} Stressing a 70-30 brass rod to produce a permanent set of only 0.006 per cent dropped the 0.0002 per cent "offset proportionality limit"* from 23,000 lb. per sq. in. to 14,500 lb. per sq. in., and further straining up to 35 per cent permanent elongation left the proportionality limit at 8000 to 10,000 lb. per sq. in. These data are shown in Fig. 13. The 0.01 per cent offset stress decreases with prior extension up to 10 per cent and increases thereafter; this being

* The offset proportionality limit is the stress required to cause a specified deviation from the modulus line.

so, it appears likely that the 0.0002 per cent offset strength might likewise increase at some greater prior permanent extension.

Orowan¹³ gives still other examples of the effect of straining on the mechanical properties of single crystals.

SUMMARY

Minor Constituents.—An addition of 0.012 per cent of soluble elements to the high-purity copper was sufficient to increase the life twenty-fold (Table 2). The role played by soluble constituents in increasing the life is not clearly understood. The increased resistance to fracture of an oxygen-free copper containing soluble impurities appears to be related to the higher softening temperature. However, the effect is partly due to the smaller grain size of the impure copper.

The presence of oxygen in the copper introduces other factors. Furnace-cooled oxygen-bearing copper was found to have a shorter life in rupture (at the same stress) than oxygen-free copper of the same general composition.

The role of oxygen in reducing the life of an alloy copper appears to be one of purification of the copper matrix. In a furnace-cooled tough-pitch copper some impurities exist primarily as oxides, leaving a purer copper matrix of lower resistance to rupture than copper containing dissolved elements. Water quenching, on the other hand, retains the elements in solution, so that very little difference exists between the life of quenched oxygen-bearing and quenched oxygen-free copper of the same general analysis. The net effect of oxygen in an impure copper is to decrease the effect of cooling rate on the life under sustained loads.

Cooling Rate.—It has been observed that great changes in the rupture life of copper at 200°C. are caused by varying the rate of cooling from the annealing temperature (Figs. 1 to 8). Specifically, the faster the cooling rate, the shorter the life and the

lower the ductility. This effect was found for a wide variety of coppers, including spectrographically pure copper (99.999+ per cent), and applies likewise for silver.

The experimental data are explained by the hypothesis that attributes the effect of cooling rate to variations in the degree of perfection of the atomic arrangement. Water quenching retains imperfections in the lattice which were generated at high temperatures by thermal fluctuations; furnace cooling permits the atoms to become more perfectly arranged with fewer lattice imperfections. Such imperfections or dislocations are assumed to be responsible for the weakness of metal crystals, and consequently the material containing the greatest number of free dislocations should have the shorter life; i.e., the water-quenched copper.

Variations in the rate of cooling from the annealing temperature also influenced the creep characteristics and the internal friction of the copper.

Effect of Cold-work.—Small degrees of cold-work prior to testing were found to decrease the rupture life of furnace-cooled copper. Beyond a certain degree of deformation, the life was increased by cold stretching. This information on "strain-weakening" agrees with previous work by Smith,^{11,12} Orowan,¹³ and Read.¹⁰ In other words, plastic deformation does not always increase the resistance of a metal to further deformation, but may actually produce a condition more favorable for slip.

ACKNOWLEDGMENT

The authors take great pleasure in expressing their indebtedness to Mr. W. E. Ruder for initiating this program, and for his counsel and guidance.

We also wish to make due acknowledgment to Messrs. J. S. Smart, Jr. and A. A. Smith, Jr., of the American Smelting and Refining Co., Barber, N. J., and to Dr. Roman Smeluchowski, Research Labora-

tory, General Electric Co., for many interesting and helpful discussions.

Our thanks also to the Metallurgical Section of the Pittsfield Works' Laboratory of the General Electric Co.; in particular to Messrs. C. H. Hannon and R. Ward for materials and discussions and to Mr. D. H. Connor for determining the softening temperatures of the coppers.

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DISCUSSION

(H. L. Burghoff presiding)

A. A. SMITH, JR.,* Barber, N. J.—The authors have presented some very interesting and useful data on the properties of copper and they are to be highly congratulated. We have all too little information on the properties of

copper at slightly elevated temperatures and this work is a very welcome addition.

It will be noted that No. 7, which is a synthetic, oxygen-free copper, and No. 4 which is a tough-pitch copper, have very nearly the same impurity contents except for the oxygen. However, there is a considerable difference in the rupture properties, the oxygen-free material being better at all stresses.

Turning to No. 2, which is a silver-bearing oxygen-free copper, and to No. 5, which is a silver-bearing tough-pitch copper, it will be noted that the reverse appears to be true; that is, the tough-pitch copper appears to be the better. There is some difference in the silver content of these two coppers; the oxygen-free has the higher amount, which might be expected to further accentuate differences but which does not do so.

I wonder if the authors might have some explanation of the fact that in one case oxygen has a beneficial effect and in the other an adverse effect.

H. L. BURGHOFF,* Waterbury, Conn.—I should like to ask the authors if they have considered quenching strains as a possible factor in the observed differences between the quenched and the furnace-cooled materials.

Another matter that merits discussion concerns the initial extension that occurs immediately upon application of the test load. As most of the stresses applied in the authors' tests were well above the nominal yield strength of annealed copper at 200°C., the instantaneous elongations must have been considerable and, conceivably, a factor in the test results. I wonder if the authors have a record of those initial extensions and if they have considered what their effect may be.

D. K. CRAMPTON,† Waterbury, Conn.—I was very much interested in the observations that metallic impurities dissolved in the matrix usually materially improve the rupture strength. This might be taken as evidence of the falsity of the assumption all too commonly made that high purity in metals and alloys necessarily results in high quality or better properties. There are many other indications

* Chase Brass and Copper Company.

† Director of Research, Chase Brass and Copper Company.

* American Smelting and Refining Company.

that this idea is erroneous. It is hoped the authors will continue this study and perhaps make a systematic investigation of various dissolved metallic impurities over a considerable range.

I wish to ask the authors one question; i.e., whether the factors are progressive more or less from the start of exposure or whether they occur rather rapidly after a certain period of time.

D. L. MARTIN and E. R. PARKER (authors' reply).—The variations pointed out by Mr. Smith are probably due to differences in grain size and not to any effect of oxygen. The silver-bearing tough-pitch copper (No. 5) has a finer grain size (Table 3) than the silver-bearing oxygen-free copper (No. 2) and therefore should be stronger, in view of the results in Table 4, which show a fine-grained copper to have a greater resistance to rupture at 200°C. than a coarse-grained copper. However, it seems likely that for a constant grain size the copper containing oxygen will have a shorter rupture life than an oxygen-free material, owing to inclusions or to purification resulting from oxidation.

Dr. Burghoff has inquired about the possible effect of quenching strains in regard to explaining the observed effect of cooling rate. We found that samples furnace-cooled at a rate of 25°C. per hour had a longer rupture life at 200°C. than samples cooled 100°C. per hour (Table 7). It is inconceivable that there could have been quenching strains in either sample, therefore some factor other than quenching strain was operating to produce the changes.

The hypothesis advanced in the paper is open to question, of course. Dr. Burghoff has mentioned the initial extension of the bars as a factor that should be discussed. When the bar is loaded, there occurs an instantaneous

elongation of considerable magnitude. For example, in Fig. 12 the initial extension is shown to be over 10 per cent. It would seem that atomic changes occurring during the initial extension would mask out any structural changes produced by a variation in the cooling rate. Apparently that does not occur, for the effect of the final cooling treatment persists after the loading of the bar. Therefore, it appears that the initial variations in the degree of perfection of the atomic arrangement due to variations in the prior cooling treatment are not changed by the deformation that results when the bars are loaded.

TABLE 7.—*Effect of Variations in Cooling Rate on the Rupture Life of High-purity Copper at 200°C.*

Treatment (Bars Were Annealed at 850°C.)	Stress, Lb. per Sq. In.	Life, Hr.	Elongation, Per Cent in 1 In.	Reduction of Area, Per Cent
Water-quenched.....	15,750	6		18
Furnace-cooled 100°C./hour.....	15,750	46	14	30
Furnace-cooled 25°C./hour.....	15,750	74	13	35

In connection with Dr. Crampton's question, we have found that microscopic cracks do not start to form until the final stage of creep prior to rupture. However, it is likely that defects are forming in the grain boundaries at all stages but that they are too small to detect under the microscope. The strengthening effect of alloying elements and the effect of cooling rate is evident from the time the load is first applied. In Fig. 12, for example, the water-quenched sample has a much higher creep rate at all stages of the test than has the furnace-cooled copper.

High-speed Tensile Impact Tests on Single-crystal and Polycrystalline Bars of Copper

By E. R. PARKER,* JUNIOR MEMBER A.I.M.E., AND E. A. SMITH*

(New York Meeting, February 1944)

METALLURGISTS and engineers have always been interested in the mechanism of high-speed deformation because metals are rapidly deformed in various applica-

Single-crystal copper specimens were broken in tension at impact velocities up to 100 ft. per sec. The distribution of slip bands in the fractured crystals was

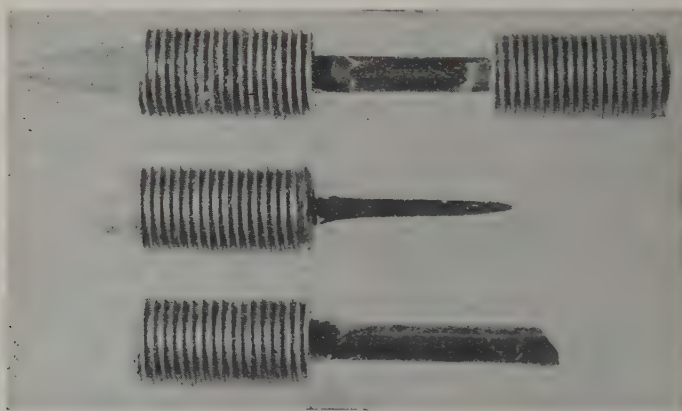


FIG. 1.—SINGLE-CRYSTAL TEST BAR SHOWING THREADED BUSHINGS SILVER-SOLDERED TO CRYSTAL WITH TWO VIEWS OF A FRACTURED CRYSTAL.

tions and manufacturing processes. The deformation of metals by impact loads has recently engaged the attention of a number of investigators. Many of their results have not been disclosed but some of the published investigations¹⁻⁸ have shown that the tensile strength, yield strength and elongation generally increase with increasing strain rate. The investigation reported herein is an attempt to determine the reason for this increase in strength and elongation.

found to depend upon the strain rate. In the bars broken at high speeds, the slip bands appear to be more numerous. This might account for the higher strength as well as the greater elongation.

EXPERIMENTAL PROCEDURE

Single crystals of copper (approximately 99.98 per cent) were made in graphite molds by the conventional method of lowering the mold out of the hot zone of a hydrogen furnace at a rate of one inch per hour. Solidification progressed from the bottom upward, forming a single crystal. The crystals were about 0.30 in. in diameter and 4 in. long. They were

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* Research Laboratory, General Electric Co., Schenectady, N. Y.

¹ References are at the end of the paper.

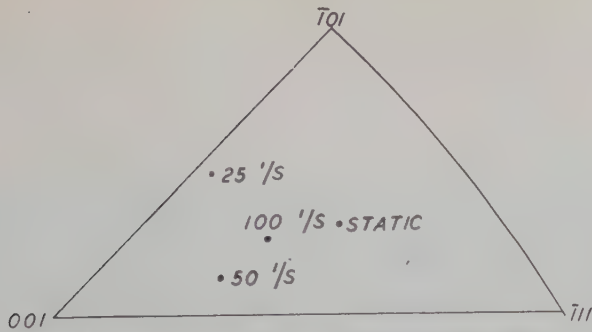


FIG. 2.—STEREOGRAPHIC PLOT OF AXES OF CRYSTALS.

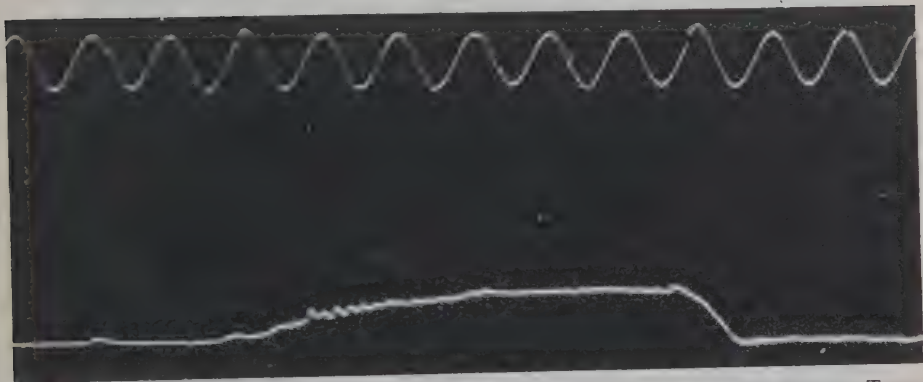


FIG. 3.—STRESS-TIME RECORD FOR SINGLE CRYSTAL BROKEN AT 25 FEET PER SECOND. TIMING WAVE IS 2000 CYCLES PER SECOND.

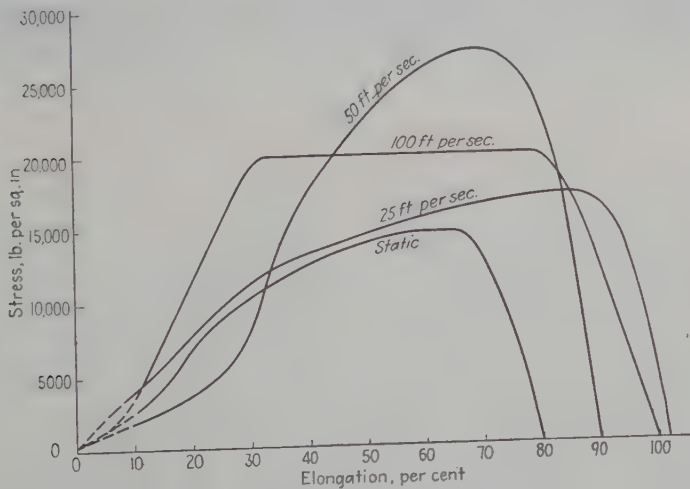
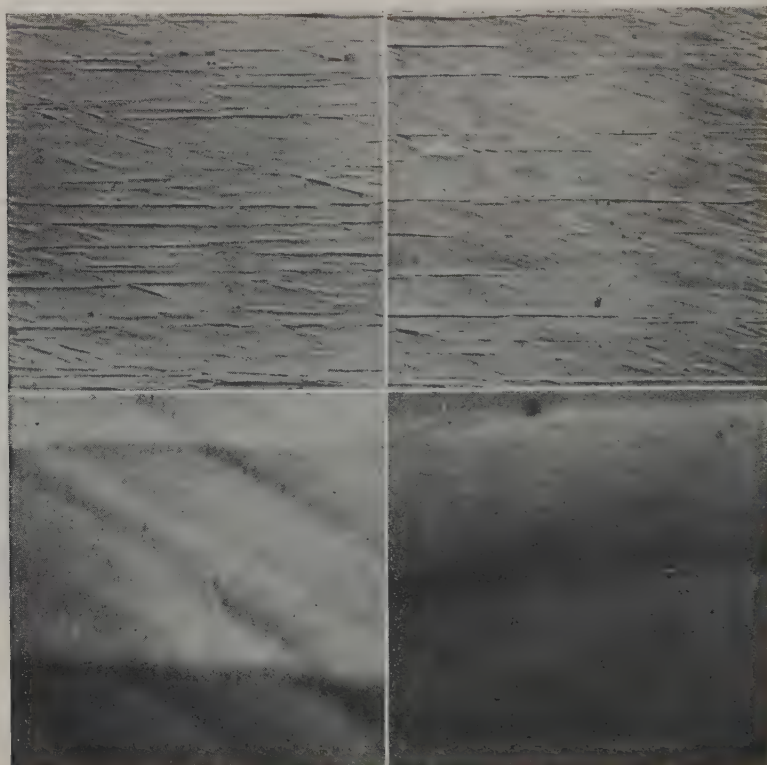


FIG. 4.—TENSILE-STRESS TENSILE-STRAIN CURVES FOR SINGLE CRYSTALS BROKEN AT DIFFERENT IMPACT VELOCITIES.

made into test bars by sliding threaded steel bushings over each end of a crystal and then flowing silver solder between the crystal and the bushing. The inside

specimen is indicated on a standard projection. The bars were broken in a commercial variable-velocity tension impact machine, which has been described



Static

25 Ft. per Second

FIG. 5.—SLIP BANDS ON CRYSTALS
Above, photomicrographs. $\times 500$. Below, electron

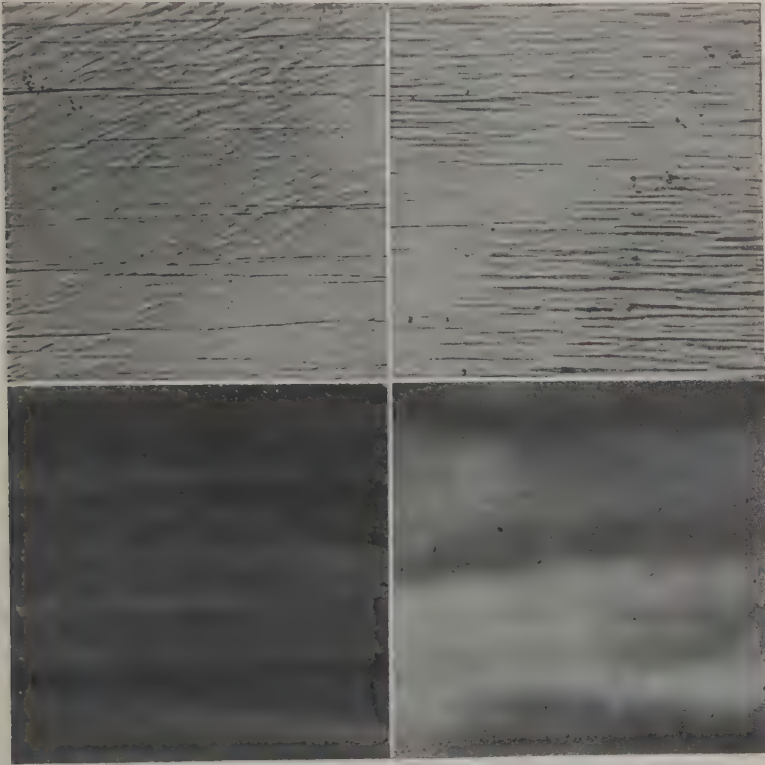
diameter of the bushings was slightly greater than the diameter of the crystals, to allow space for the silver solder. The bushings were placed so that the gauge length of the crystals was one inch. The assembly is shown in Fig. 1, with two views of a fractured crystal. Annealed polycrystalline copper bars of similar shape were machined from solid stock. X-ray measurements were made on all single crystals to determine their orientations. The results are shown in Fig. 2, where the location of the axis of each

in detail elsewhere.^{7,8} The stress and strain were recorded by means of wire strain gauges and a special commercial oscillograph, also described in detail elsewhere.^{9,10}

The equipment and method can be briefly described as follows. The impact machine consists of a motor-driven flywheel containing a two-pronged hammer. This hammer is held retracted in the flywheel until the desired impact speed is reached, then it is released to strike a cross arm screwed on one end of the specimen. The other end of the specimen is screwed into

a heavy ballistic pendulum and consequently is held essentially stationary while the bar is being broken. From the swing of the ballistic pendulum the energy

extension arm and the test bar. In the stress calculations the oscillating component of stress must be neglected, and only the steady component calculated



50 Ft. per Second

100 Ft. per Second

BROKEN AT VARIOUS IMPACT VELOCITIES.
micrographs. $\times 5000$. (Formvar replica method.)

absorbed by the bar during fracturing can be calculated.

For measuring stress, a wire strain gauge was placed on the extension arm connecting the test bar and the pendulum. Previously reported experiments¹⁰ had shown that if certain precautions are taken the stress measured in this way agrees very well with the stress measured on a large-diameter portion of a special test bar having large and small sections. The oscillations of stress set up by the shock waves, however, differ considerably in the

from the records for the stress-strain curves. The strain was measured by the change in resistance of a wire stretched parallel to the axis of the test bar. The flywheel was so large that the front end of the test bar came up to speed very quickly and the strain was found to be proportional to time except for a relatively short time interval immediately following the impact.

The output from the strain gauges was amplified and fed into special cathode-ray oscillographs. The trace of the beam was

photographed with a high-speed camera. A timing wave of 2000 cycles per second was photographed simultaneously.

Before testing, the single-crystal speci-

more generally in the high-speed tests. This might account for the observed increase in elongation. The electron micrographs are valuable for studying

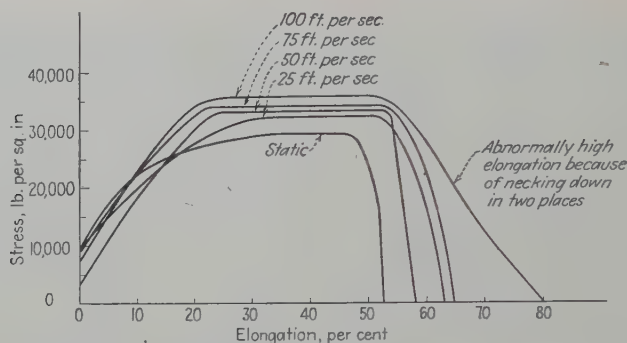


FIG. 6.—TENSILE STRESS-STRAIN CURVES FOR POLYCRYSTALLINE BARS BROKEN AT DIFFERENT IMPACT VELOCITIES.

mens were polished electrolytically by Jacquet's¹¹ method, so that the distribution of slip bands in the fractured crystals could be studied.

RESULTS

One of the stress-time records is shown in Fig. 3. Tensile-stress and tensile-strain curves were calculated from the steady component of stress using the original cross-sectional areas of the bars. These curves are shown in Fig. 4 for single crystals broken at impact velocities of 0, 25, 50 and 100 ft. per sec. Before a direct comparison could be made it would be necessary to know the resolved shear-stress vs. shear-strain curves. Even from the tensile stress-strain curves, however, the increase in elongation with the speed of fracture is evident.

The surfaces of the broken bars were examined microscopically. The distribution of slip bands appeared to vary with impact velocity. Fig. 5 shows the photomicrographs of the slip bands. A comparison of the samples, particularly the one broken statically and the one fractured at 100 ft. per sec., indicates that deformation occurs

the shape of the slip bands but not for studying the distribution, because of the small area visible at such high magnification. In the electron micrographs, the bands appear to increase in width as the impact velocity increases, indicating that more planes function in each band. These observations were verified by testing and examining a duplicate set of crystals.

The results obtained with polycrystalline bars are in good agreement with those obtained with single crystals. The stress-strain curves shown in Fig. 6 clearly illustrate the increase in tensile strength that occurs when bars are broken at high strain rates. The elongation values for bars broken at high speeds are consistently greater than the static elongation but there is some scatter in the values. The bar broken at 50 ft. per sec. had a slightly lower elongation than the bar broken at 25 ft. per sec. The polycrystalline bars were marked at short intervals along the gauge length, so that the general elongation of the bars away from the fracture, as well as the total elongation, could be measured. The results obtained for general and total elongations are listed

in Table 1. From these it is evident that bars broken at high speeds undergo greater general elongation than bars fractured statically. This is in agreement with the observations on single crystals, which showed that more slip occurred in the rapidly deformed crystals. The energy required to rupture the polycrystalline bars was obtained by integrating the area under the stress-strain curves. These values agreed reasonably well with the energy calculated from the swing of the ballistic pendulum.

DISCUSSION OF RESULTS

Without going into the details of the mechanism of deformation and shock-wave analysis in high-speed impact tests, it is possible to obtain some plausible correlations between the observed phenomena.

It appears that a greater number of slip planes function in the operating slip systems when crystals are broken by rapidly applied loads. If the same amount of strain occurs in each slip band, the greater number of operating bands could account for the increased elongation.

TABLE 1.—*Elongations*

Impact Velocity, Ft. per Sec.	General Elongation, Per Cent	Total Elongation, Per Cent
0	45	52.5
25	53	63
50	52	58
75	54	65
100	58	80 ^a

^a The elongation of the specimen broken at 100 ft. per sec. is abnormally high because "necking down" occurred at two places. Double necking has been observed before and is not uncommon. It does, however, illustrate the tendency toward greater general elongation, characteristic of bars broken at high speeds.

In the crystals broken at high speeds, the slip bands seem to be much closer together. Consequently, the material has undergone more strain per unit volume, therefore it is reasonable to expect a

greater degree of strain-hardening and thus a higher strength.

It is hoped that further research will enable experimenters to determine quantitatively the connection between the density of slip bands and mechanical properties.

At the present time, there is an incomplete understanding of the mechanism by which more slip bands form during the high-speed tests. Theories concerning their formation may be evolved as research in this field progresses.

ACKNOWLEDGMENTS

The authors are grateful to many of their associates for helpful cooperation and contributions to this investigation—to Messrs. M. D. Collins and R. L. Adams for making the single crystals, to Mrs. C. B. Brodie for the photomicrographs, to Dr. Harker, Miss M. J. Murphy, Mr. E. T. Asp and Mrs. B. F. Decker for the electron micrographs and orientation determinations, and to Mr. D. J. De Michael for assistance with the oscillographic records. Their appreciation is extended also to Mr. W. E. Ruder, in charge of metallurgical research, for sponsoring and making possible this investigation.

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Solubility of Hydrogen in Molten Copper-tin Alloys

By MICHAEL B. BEVER,* JUNIOR MEMBER, AND CARL F. FLOE,† MEMBER A.I.M.E.

(New York Meeting, February 1944)

THE solubility of hydrogen in molten copper-tin alloys is of both practical and theoretical interest. From a practical standpoint, data on the equilibrium solubility as a function of temperature, pressure and alloy composition are valuable for a better understanding of porosity problems in bronze castings. From the theoretical point of view the determination of the hydrogen-copper-tin equilibrium is of interest since it extends the laws governing the solution of gases in metals.

This paper presents the results of an investigation of the solubility of hydrogen in representative compositions of the copper-tin system at temperatures ranging from above the liquidus to 1300°C. and at pressures from less than 50 mm. of mercury to about atmospheric.

REVIEW OF PREVIOUS WORK

The solubility of hydrogen in copper was determined by Sieverts and Krumbhaar¹ in 1910 and by Roentgen and Moeller² in 1934. Their values are in fair agreement. In 1926 Iwasé³ reported results that were very much higher.

The published data on the solubility of

hydrogen in tin do not agree. Smithells⁴ states that no reliable data are available. According to Sieverts and Krumbhaar,⁵ hydrogen is insoluble in tin. Bircumshaw,⁶ on the other hand, found a definite solubility at 800°C. The latter's experimental procedure did not provide for stirring of the metal and in his opinion he failed to reach equilibrium. Iwasé³ again reported large solubility values.

For copper alloys, Sieverts and Krumbhaar⁵ distinguished between alloying elements that do not markedly affect the solubility of hydrogen, elements that increase the solubility, and elements that reduce it. They named gold, tin, and aluminum as examples of this last group and reported hydrogen solubility data at 1225°C. for the copper-rich side of these alloy systems at atmospheric pressure. Without giving experimental results, they stated that the amount of hydrogen dissolved by liquid copper alloys is proportional to the square root of the pressure as in pure metals. These authors suggested that in a limited way the effect of an alloying element on the solubility of a gas is related to the constitution diagram for the alloy system. Sieverts⁷ also called attention to the fact that the curve of hydrogen solubility versus composition of copper-tin alloys shows a sharp change of direction at the composition of Cu₃Sn and suggested that this compound persists at least to some extent in the molten state.

Iwasé³ reported large hydrogen solubility values for several compositions of copper-tin alloys, which appear to be in error.

This work represents a portion of a thesis to be submitted by M. B. Bever in partial fulfillment of the requirements for the degree of Doctor of Science from the Massachusetts Institute of Technology. Manuscript received at the office of the Institute Nov. 19, 1943. Issued as T.P. 1703 in METALS TECHNOLOGY, April 1944.

* Instructor in Metallurgy, Massachusetts Institute of Technology, Cambridge, Massachusetts.

† Associate Professor of Physical Metallurgy, Massachusetts Institute of Technology.

¹ References are at the end of the paper.

In 1929 Sieverts⁸ gave a review of his earlier work on the solubility of gases in metals, including a summary of the effects of alloying elements.

EXPERIMENTAL METHODS

The apparatus used for the determination of solubility was based on a principle first developed by Sieverts. This method determines the solubility by finding the difference between the volume of soluble gas admitted to the furnace at a certain temperature and pressure and the so-called "hot volume," which is the volume of an insoluble gas necessary to fill the furnace under the same conditions. The furnace and accessory equipment used were similar to those described by Floe and Chipman.⁹ By using capillary tubing and charging the furnace to capacity it was possible to keep the hot volume low. In none of the runs did it exceed 20 c.c. and in most runs it was of the order of 12 to 14 c.c. This represents a substantial reduction from the hot volumes used by other investigators. A low hot volume is desirable because it increases the accuracy of the solubility determinations.

The procedure for making solubility determinations was essentially the same as that described by Floe and Chipman,⁹ but because of the small solubilities involved in many instances, special precautions had to be taken. The molten alloys were first thoroughly deoxidized with hydrogen, then the hot volume was determined with nitrogen, which is insoluble in both copper and tin. Some hot volumes were checked with argon and helium and satisfactory agreement was obtained. Within the limits of observation the hot volume was found to be a straight-line function of temperature.

In some instances the hot volume underwent a small change during a run, probably owing to one or both of two causes. First, if a metal deposit formed along the upper walls of the crucible, due to condensation or splashing of the metal, the temperature distribution in the gas space, and conse-

quently the hot volume, would change. Second, it was found that if the crucible had plane surfaces and was kept under vacuum at high temperatures for extended periods, these surfaces were inclined to change permanently by curving inward.

It is well known that hydrogen diffuses through fused silica at the temperature of molten copper.¹⁰ The effects of such diffusion were noticeable if hydrogen was left in the furnace for extended periods. However, since equilibrium was obtained very rapidly, the data reported here were not affected by the diffusion loss to a significant degree.

The copper used was high-purity electrolytic sheet prepared by the method of Smart, Smith and Phillips.¹¹ In addition to negligible amounts of occluded electrolyte, the impurity contents stated in Table I of their paper are believed to apply to this material. The tin was analyzed chemically pure grade with total reported impurities less than 0.007 per cent. Tank gases were used with a purity of 99.5 per cent for nitrogen and 99.95 per cent for hydrogen. The argon used was reported to analyze 99.4 per cent argon and 0.6 per cent nitrogen.

The metals were cut to fit the crucible, and cleaned by pickling. They were charged to the crucible in as compact a manner as possible and the furnace was sealed. It was found feasible to make the alloys in the furnace by charging weighed amounts of copper and tin. One low-tin and one high-tin alloy were analyzed and the compositions were found to agree with the charge calculations within the probable analytical errors. The amount of metal charged varied between 120 and 215 grams.

Temperatures were read on an accurate potentiometer, which was connected to a platinum-platinum-rhodium thermocouple. The freezing points of copper and tin were used for calibration. The temperature of the bath, which was heated by induction, could be controlled within $\pm 2^\circ\text{C}$. The stirring action of the induction heating accelerated the attainment of equilibrium.

RESULTS OF EXPERIMENTAL WORK

The solubility of hydrogen in pure molten copper as a function of temperature at one

solubility of hydrogen in pure copper as a function of pressure at 1200°C. is shown by the uppermost curve in Fig. 2; the observed values are tabulated in Table 2.

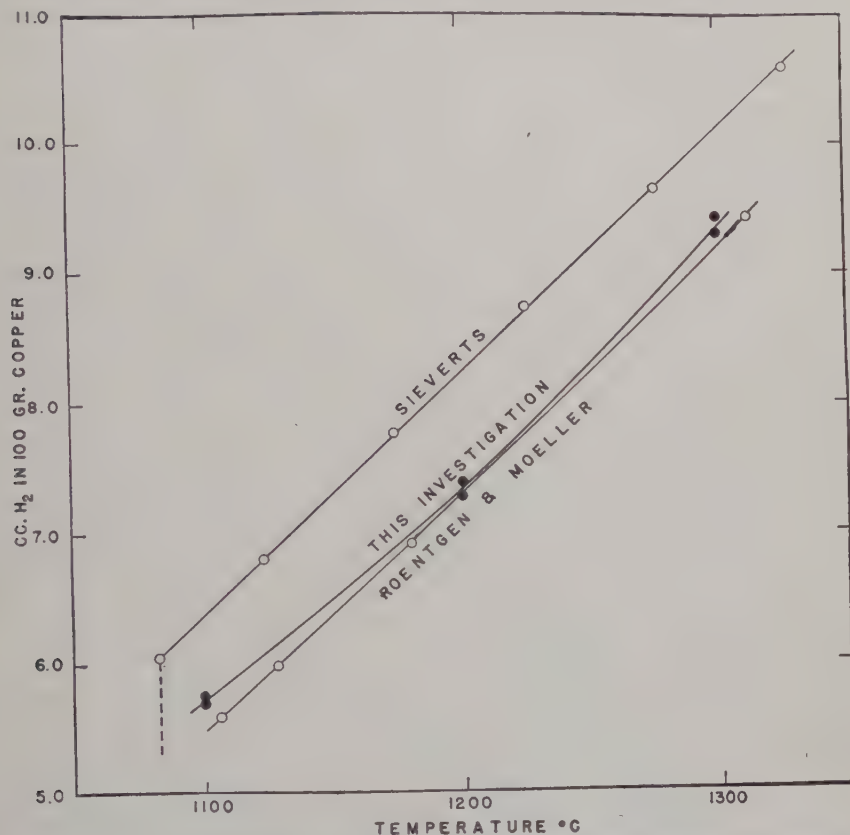


FIG. 1.—SOLUBILITY OF HYDROGEN IN MOLTEN COPPER AT ONE ATMOSPHERE PRESSURE AS A FUNCTION OF TEMPERATURE.

atmosphere pressure is shown in Table 1 and in Fig. 1. Data reported by Sieverts³ in

TABLE 1.—*Solubility of Hydrogen in Pure Copper at One Atmosphere Pressure and Various Temperatures*

CUBIC CENTIMETERS PER 100 GRAMS COPPER

Run No.	1100°C.	1200°C.	1300°C.
13	5.76	7.28	9.31
15	5.70	7.39	9.43

TABLE 2.—*Solubility of Hydrogen in Pure Copper at 1200°C. and Various Pressures*

Run No.	Pressure, Mm. Hg	H ₂ per 100 Grams Metal, C.C.
13	59.1	1.95
	106.4	2.75
	220.6	3.94
	430.5	5.44
	548.0	6.16
15	756.7	7.36
	101.4	2.62
	193.9	3.66
	313.4	4.62
	435.9	5.52
	579.6	6.40
	671.6	7.01
	750.6	7.46

1929 and the results of Roentgen and Moeller² are also included in Fig. 1. The

Table 3 lists the measured solubilities of hydrogen in pure tin as a function of temperature at one atmosphere pressure. This

lated in Table 4 and are included in Fig. 2. In Fig. 3 the solubility of hydrogen in the different copper-tin alloys at one atmos-

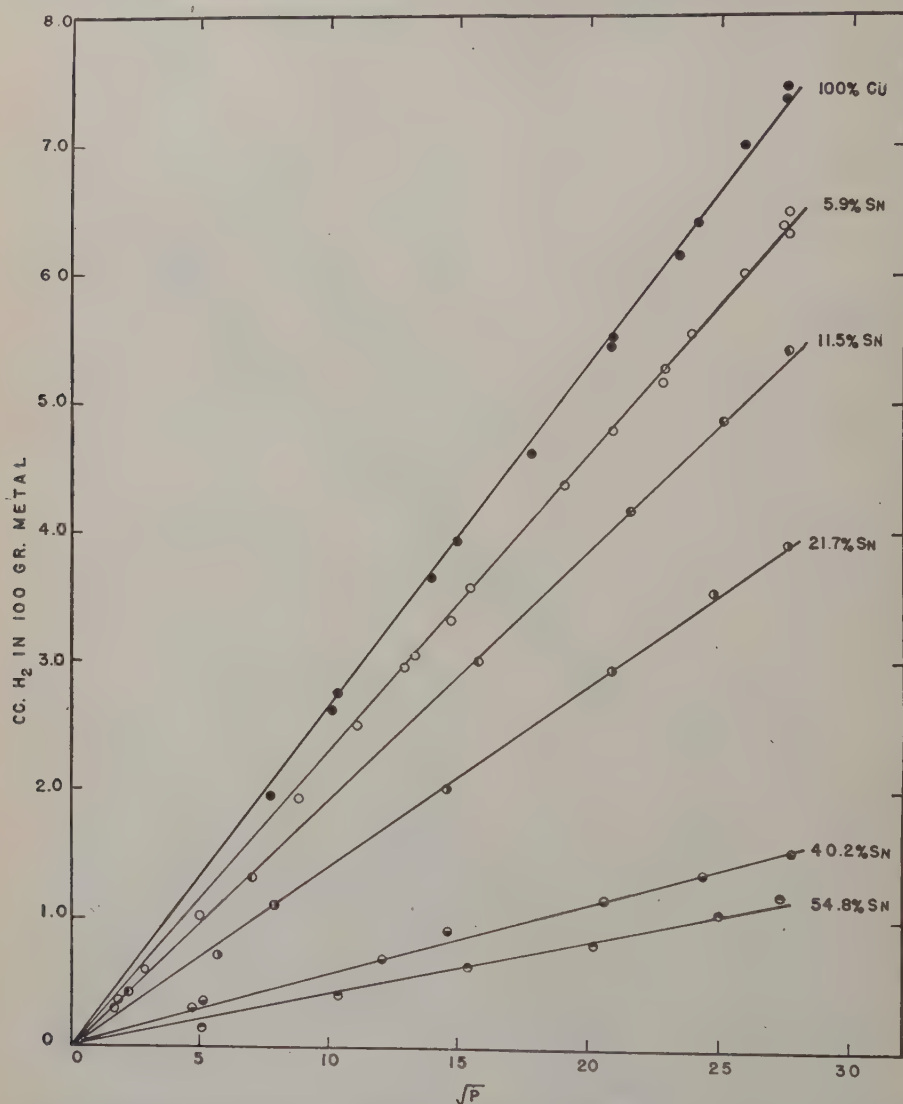


FIG. 2.—SOLUBILITY OF HYDROGEN IN COPPER AND COPPER-TIN ALLOYS AT 1200°C. AS A FUNCTION OF PRESSURE (MM. Hg).

solubility was too small to permit an investigation of the effect of pressure.

The observed values for the solubility of hydrogen in different copper-tin alloys as a function of pressure at 1200°C. are tabu-

phered pressure has been plotted as a function of temperature.

Table 5 and Fig. 4 show the solubility of hydrogen at one atmosphere pressure versus alloy composition for different tempera-

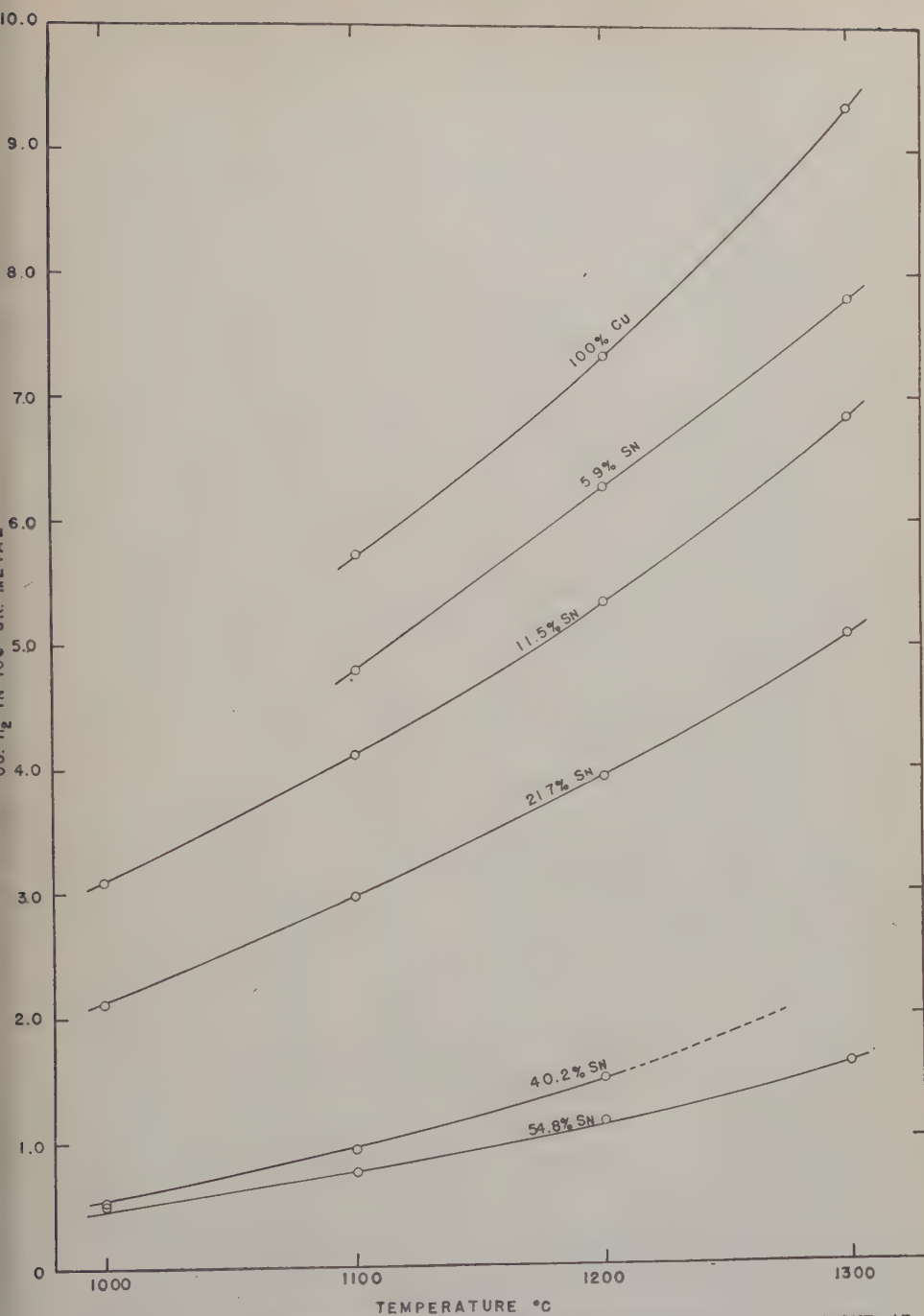


FIG. 3.—SOLUBILITY OF HYDROGEN IN MOLTEN COPPER AND COPPER-TIN ALLOYS AT ONE ATMOSPHERE PRESSURE AS A FUNCTION OF TEMPERATURE.

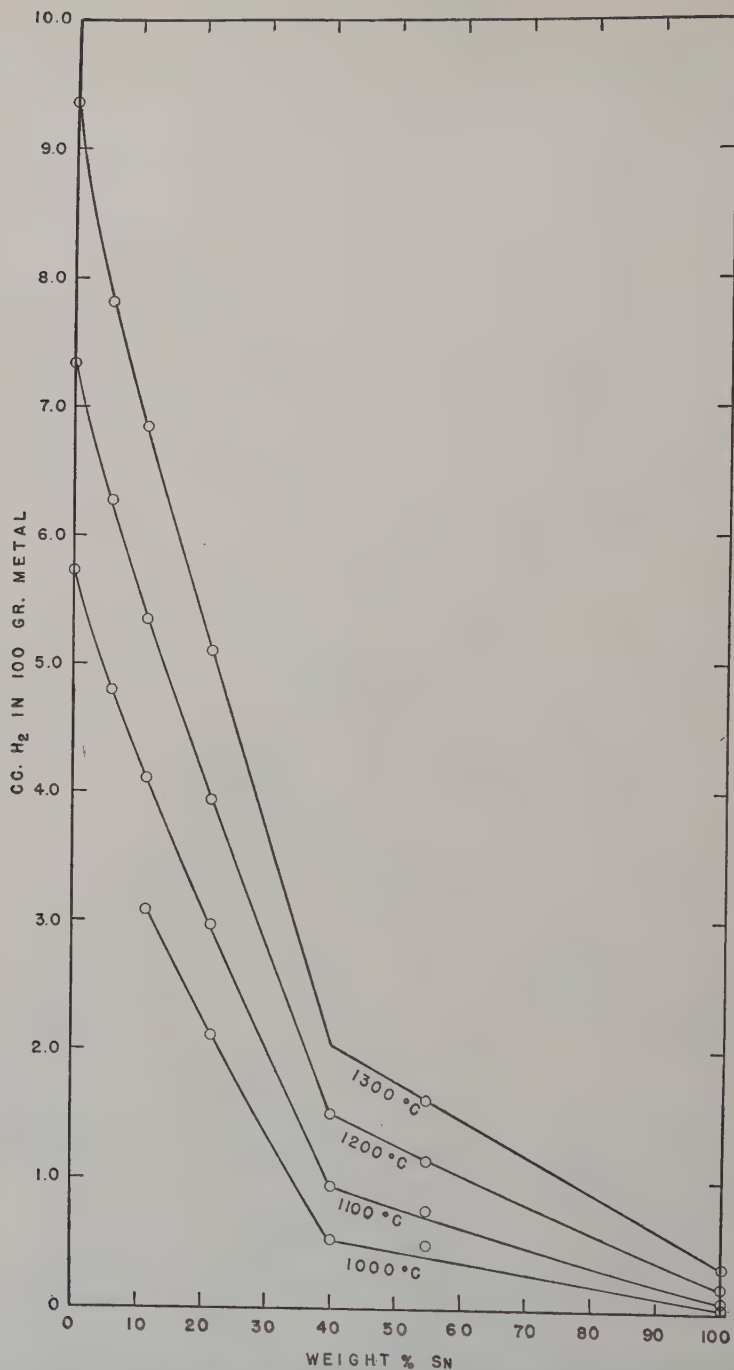


FIG 4.—SOLUBILITY OF HYDROGEN IN MOLTEN COPPER-TIN ALLOYS AT ONE ATMOSPHERE PRESSURE AS A FUNCTION OF ALLOY COMPOSITION.

tures. The units used in Fig. 4 are cubic centimeters of hydrogen dissolved in 100

TABLE 3.—*Solubility of Hydrogen in Pure Tin at One Atmosphere Pressure and Various Temperatures*
C.C. H₂ IN 100 GRAMS

Run No.	1000°C.	1100°C.	1200°C.	1300°C.
7	0.06		0.20	
8		0.11	0.21	0.28
17	0.02	0.09	0.21	
18		0.07	0.20	0.43

grams of metal versus weight per cent of tin in the metal. Fig. 5 presents the measured values of cubic centimeters of hydrogen per

TABLE 4.—*Solubility of Hydrogen in Copper-tin Alloys at 1200°C. and Various Pressures*

Run No.	Sn, Per Cent	Pressure, Min. Hg	H ₂ per 100 Grams Metal, C.C.
12	5.9	3.4	0.36
		25.3	1.02
		166.3	2.95
		236.8	3.57
		362.6	4.37
		524.3	5.28
		672.6	6.01
		750.6	6.38
		2.9	0.29
		123.6	2.50
10	5.9	177.2	3.06
		437.6	4.80
		569.7	5.54
		761.8	6.49
		8.6	0.59
		78.0	1.93
		217.7	3.32
		518.9	5.17
		760.6	6.32
		5.0	0.41
6	11.5	49.8	1.31
		247.7	3.04
		468.1	4.17
		626.8	4.87
		763.1	5.42
		62.8	1.10
		211.6	2.09
		437.6	2.94
		614.2	3.54
		764.0	3.91
14	21.7	33.0	0.71
		764.0	3.91
		26.5	0.35
		213.0	0.91
		423.1	1.16
		590.5	1.36
		771.2	1.53
		146.1	0.69
		22.6	0.30
		26.2	0.15
3	40.2	108.3	0.40
		237.4	0.64
		404.0	0.81
		624.3	1.05
		745.4	1.19
16	54.8	26.2	0.15
		108.3	0.40
		237.4	0.64
		404.0	0.81
		624.3	1.05
		745.4	1.19

1 gram mol of metal versus atomic per cent of tin in the metal. All hydrogen volumes are reduced to standard temperature and pressure.

TABLE 5.—*Solubility of Hydrogen in Copper-tin Alloys at One Atmosphere Pressure and Various Temperatures*
C.C. H₂ IN 100 GRAMS ALLOY

Run No.	Wt. Per Cent Sn	At. Per Cent Sn	1000°C.	1100°C.	1200°C.	1300°C.
10, 12	5.9	3.3		4.80	6.28	7.81
6	11.5	6.5	3.09	4.11	5.35	6.85
14	21.7	12.9	2.11	2.97	3.94	5.10
3	40.2	26.4	0.53	0.94	1.50	
16	54.8	39.3	0.50	0.76	1.15	1.61

DISCUSSION OF RESULTS

The values for the solubility of hydrogen in pure copper at one atmosphere pressure agree closely with those reported by Roentgen and Moeller and are about 10 per cent lower than those of Sieverts. In the range covered the solubility is approximately a straight-line function of temperature. However, the measured values do not conform as closely to a straight line as do those of other investigators, but give a curve of slowly increasing slope. Fig. 3 shows similar upward curves for the hydrogen solubilities in the various copper-tin alloys investigated.

The solubility of hydrogen in copper as well as in copper-tin alloys determined at 1200°C. is proportional to the square root of pressure within the limits of experimental error. Sieverts' law, which was discussed in detail by Floe and Chipman,⁹ is thus obeyed.

The experiments on the solubility of hydrogen in pure tin indicate definite though very small solubilities. This result is in disagreement with the work of Sieverts and Krumbhaar,⁵ who reported that hydrogen is insoluble in tin. On the other hand, the measured solubilities are only about one tenth as large as the values of Iwasé.³ His work, which also includes data

on the solubility of hydrogen in a few copper-tin alloys, apparently was affected by some fundamental error, and therefore does not warrant discussion. Bircumshaw⁶ found

These values also exceed the probable effects of diffusion and of any difference in the thermal properties of hydrogen and nitrogen. They are, however, of negligible

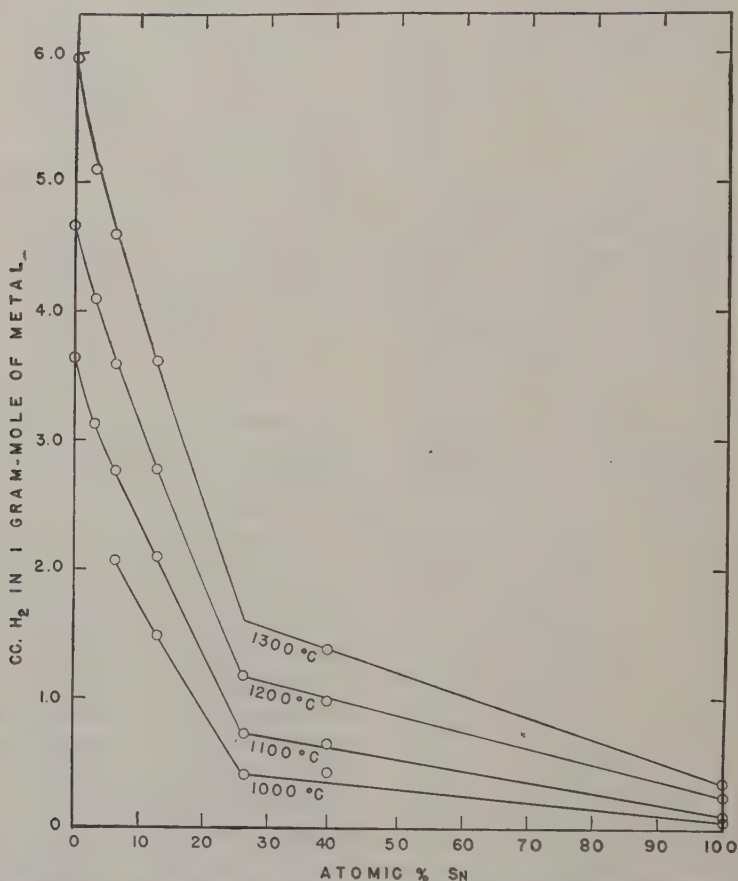


FIG. 5.—SOLUBILITY OF HYDROGEN IN MOLTEN COPPER-TIN ALLOYS AT ONE ATMOSPHERE PRESSURE AS A FUNCTION OF ALLOY COMPOSITION.

a solubility of about 0.3 c.c. of hydrogen in 100 grams of tin at 800°C., but he considered his work as inconclusive owing to failure to establish equilibrium.

In evaluating the determinations of hydrogen solubility in pure tin reported here, the values measured at 1100°, 1200°, and 1300°C. are larger than the probable combined errors in the measurement of volumes, pressures, and temperatures.

magnitude compared with the solubilities in copper and copper-tin alloys.

The solubility of hydrogen in copper-tin alloys as a function of alloy composition decreases with increasing tin content. In conventional units (Fig. 4) and in basic units (Fig. 5) the curves representing the functions consist of two nearly linear parts, which have considerably different slopes and intersect sharply at about 25 atomic

per cent of tin. The intersection thus lies at or close to the composition of Cu_3Sn . This same type of curve was obtained by Sieverts and Krumbhaar at 1225°C ., as

at or near the composition of Cu_3Sn . The magnetic susceptibility data of Endo, which include measurements on solid copper, the two-phase region and liquid alloys, are the

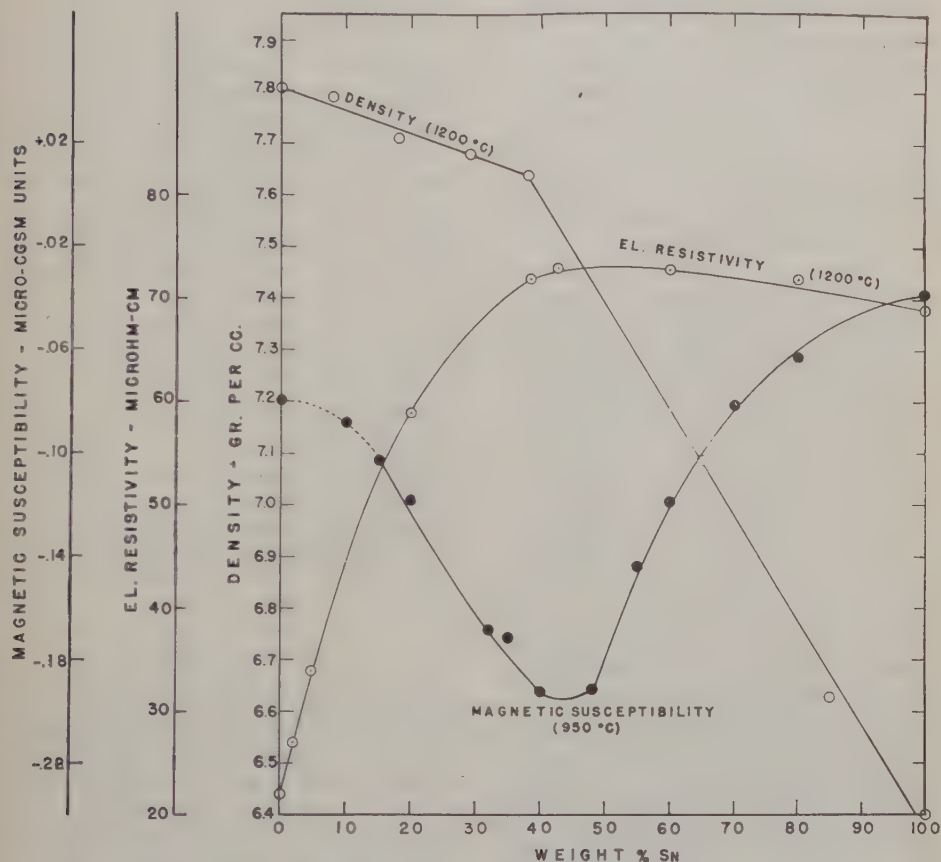


FIG. 6.—VARIOUS PHYSICAL PROPERTIES OF COPPER-TIN ALLOYS AS FUNCTIONS OF COMPOSITION.

previously noted. Their values for solubility, however, were considerably higher than those reported here.

Certain physical properties of molten copper-tin alloys are presented in Fig. 6 as functions of composition. The values are due to Bornemann and Wagenmann¹² (electric resistivity), Endo¹³ (magnetic susceptibility), and Bornemann and Sauerwald¹⁴ (density). It is evident that these properties also undergo a significant change

least decisive in this respect. Magnetic data on this system were also published by Honda and Endo.¹⁵ Bornemann and Wagenmann concluded on the basis of their electric resistivity measurements that Cu_3Sn exists in liquid copper-tin alloys. The density determinations by Bornemann and Sauerwald also point to the existence of liquid Cu_3Sn .

From the solubilities reported in Tables 1, 3 and 5, it is possible to calculate the

heats and free energies of solution of hydrogen in different compositions of the copper-tin system. The methods of calculation have been indicated in the second paper by Floe and Chipman¹⁶ on the solubility of sulphur dioxide in copper.

From a practical standpoint, it is of interest to ask whether the addition of tin to molten copper reduces the amount of hydrogen soluble in the melt to any significant extent. Table 6 shows the percentage of reduction in solubility of hydrogen when 5.9 per cent and 11.5 per cent, respectively, of tin are added to copper.

TABLE 6.—*Effect of Additions of Tin in Reducing the Solubility of Hydrogen in Copper-rich Copper-tin Alloys*

Deg. C.	Per Cent Reduction in H ₂ Solubility	
	5.9 Per Cent Sn Added	11.5 Per Cent Sn Added
1100	—16.2	—28.2
1200	—14.5	—27.2
1300	—16.7	—26.9

In spite of this reduction, however, the amounts of hydrogen that are soluble even with such low partial pressures of hydrogen as occur in furnace atmospheres are substantial, particularly in terms of actual volumes at high temperatures. While a complete quantitative understanding will also require data on the solubility of hydrogen in solid bronze, the investigation reported here points definitely to hydrogen as a major cause of porosity in bronze castings. This result confirms the work of Pearson and Baker¹⁷ on experimental castings.

SUMMARY AND CONCLUSIONS

The solubility of hydrogen in representative compositions of the copper-tin system has been studied as a function of temperature, pressure and composition. The following results were obtained:

1. The solubility of hydrogen in pure copper between 1100° and 1300°C. is nearly directly proportional to temperature. Within fairly close limits the values determined in two previous investigations were confirmed.

2. The solubility of hydrogen in pure tin is negligibly small at these temperatures. This is in disagreement with some statements in the literature.

3. The solubility of hydrogen in different liquid copper-tin alloys is a regular function of composition. It decreases rapidly with additions of tin up to approximately 40 per cent by weight or 25 atomic per cent and quite slowly with further additions. Both parts of the curve are nearly straight lines. The intersection of these lines at about 25 atomic per cent of tin is interpreted as an indication that Cu₃Sn exists in the liquid state.

4. The solubility of hydrogen in pure copper and in copper-tin alloys measured at 1200°C. is proportional to the square root of the pressure in accordance with Sieverts' law.

ACKNOWLEDGMENTS

The authors wish to acknowledge gratefully the encouragement received from Prof. John Chipman. They are also indebted to Prof. Gordon B. Wilkes for advice on temperature measurement.

Special thanks are due to the American Smelting and Refining Co. for the high-purity copper furnished for this investigation.

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DISCUSSION

(E. W. Palmer presiding)

A. J. SMITH,* Cincinnati, Ohio.—It is very gratifying to have some precise data on the solubility of bases in copper alloys. Such data are urgently needed for proper study and control of melting and casting. We ourselves, because of certain data accumulated in the past on porosity in tin-bronze castings, have somewhat discounted hydrogen rejection as a major cause of such porosity.

For many years the brass foundryman labored under great difficulties because of the erroneous idea that oxidation of the melt was responsible for porous castings. Qualitatively this misconception was dispelled a number of years ago and the paper today helps place our ideas on a quantitative basis.

Undoubtedly the causes of porosity are to be found in the collective influences of a number of factors, and I think what we shall have to do in many cases is to study the factors individually before we can make any study of their collective influence.

We need very specific data on what the gas solubilities are and how they change at the

freezing point. We learn that hydrogen is markedly soluble. We would like to know, for these copper-tin and similar alloys, just how its solubility varies with changes in the hydrogen-oxygen ratio. Only by finding exactly how much hydrogen will dissolve and how much oxygen, can we make a balance between the two. We need these very precise data right at the start.

Too many generalities have appeared in the literature, with no really substantial data to back them up.

D. R. HULL,* Waterbury, Conn.—This paper has great practical importance. I merely wish to emphasize what has already been mentioned; that is, the significance of the gas solubility change at the freezing point. It is a little bit surprising, if one is to base his views on the behavior of bronzes in actual casting, to learn that this solubility decreases with the increase of tin. The visual evidence of gas certainly increases with tin, at least up to 10 per cent tin. Since this evidence occurs mainly when the metal freezes, the inference is that the solubility of gas in solid bronze also decreases as tin increases and at a greater rate than in liquid. It all comes back to the change of solubility at the freezing point, and if the thing could be correlated with that, we might have an explanation of a great deal of practical behavior of bronzes.

C. F. FLOE (author's reply).—The experimental technique used did not permit measurement of the change in hydrogen solubility at the freezing point. However, it is believed that the major part of the hydrogen dissolved just above the freezing point is evolved during solidification, both in pure copper and in copper-tin alloys.

The visual evidence that more gas is evolved from bronze with increasing tin content, mentioned by Mr. Hull, seems to us to indicate the presence of gases other than hydrogen.

* Lunkeneimer Company.

* American Brass Company.

Preferred Orientation in Annealed 70-30 Brass Wire

By H. L. BURGHOFF,* MEMBER, AND J. S. PORTER,† JUNIOR MEMBER, A.I.M.E.

(New York Meeting, February 1944)

THIS paper presents the results of an investigation of the effect of cold-working and annealing treatments upon the occurrence of preferred orientation in annealed brass wire. The subject has received less consideration than has the same phenomenon in annealed brass sheet or strip, and perhaps very properly so in view of the obvious and undesired results obtained in the forming or drawing of strip having preferred orientation, which results are in contrast with the lack of any spectacular visual evidence in wire.

The factors of cold-working and annealing that control preferredness in strip are naturally expected to function similarly in wire. Indeed, one might expect the condition to be commoner in annealed wire, because the severity of the cold-working between anneals in commercial practice is usually much greater for wire than for strip. For example, a wire that is to be finished in the annealed condition on a diameter of 0.040 in. is commonly subjected to a final reduction of 90 per cent between the last two anneals, the large reduction being accomplished in the successive drafts of a multiple-die machine. Wire for rivets, for instance, on 0.125-in. diameter, although given a slight reduction of about 10 per cent after the final anneal, may have been given a prior reduction of 75 to 80 per cent.

Barrett¹ states the fiber axis of annealed 70-30 brass wire to be [111], with some indication of [100] as a secondary fiber axis. Croft and Sachs² have reported briefly on some differences in brass wire with random and with preferred orientations. They showed statistical plots of the twin-band angles with respect to the wire axis or direction of drawing as observed on an axial plane. They also pointed out that the resistance of the wire to corrosion-cracking when externally stressed and exposed to a mercurous nitrate solution decreased as the degree of the preferred orientation increased.

MATERIAL AND PROCEDURE

All the wire for the investigation was processed from one portion as cut for extrusion from a cast billet of the following analysis: 70.13 per cent copper; 0.01 lead; 0.01 iron; 0.02 nickel; 29.83 zinc (by difference). The billet section, 8 in. in diameter, was extruded hot to $\frac{3}{4}$ -in. diameter, after which it was processed by alternate cold-drawing and annealing treatments as indicated in Fig. 1. The earliest anneals in process were at about 1100°F. and the next to the last reductions by drawing were 58 per cent. The diameter of the finally annealed wire was 0.132 in. Semifinal anneals were at 800°F., 950°F. and 1100°F. and reductions of 47.5, 74, 83.5 and 89.5 per cent were employed in drawing to 0.132 in. The final anneals were at 875°F., 1050°F. and 1250°F. and were

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* Research Metallurgist, Chase Brass and Copper Co., Waterbury, Connecticut.

† Research Assistant, Chase Brass and Copper Co.

¹ References are given at the end of the paper.

Tensile tests were made in triplicate for both semifinal and final anneals and stress-strain curves to somewhat greater than 0.5 per cent elongation were made

when shared by an appreciable proportion of the grains in the metal, is evidenced in transverse sections, normal to the wire axis, by grains containing narrow twin

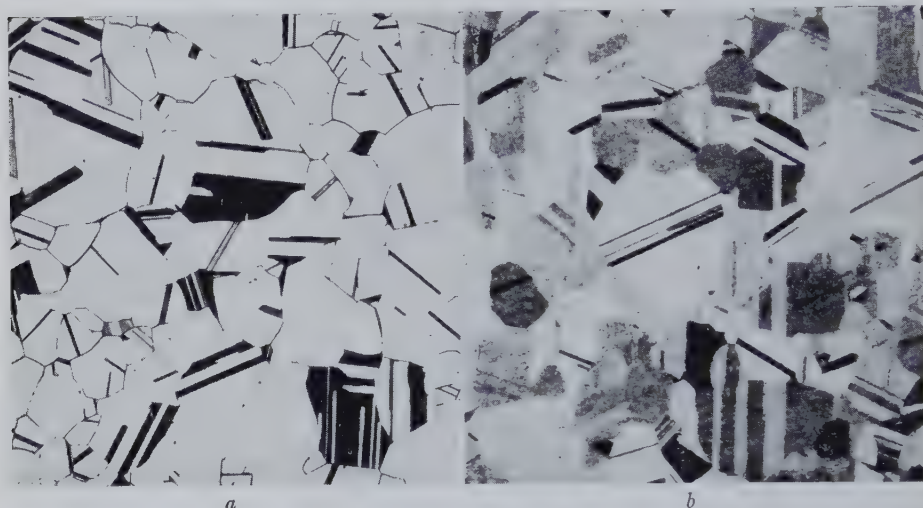


FIG. 2.—STRONGLY PREFERRED ORIENTATION IN ANNEALED 70-30 BRASS WIRE FINISHED BY THE FOLLOWING SCHEDULE:

Semi-final anneal: 800°F.
Final reduction: 74 per cent
Final anneal: 1250°F.

a. Transverse section.

b. Axial section. Drawing direction horizontal.

Etch: Ammonia and peroxide. $\times 75$.

for the latter materials by means of a Templin type recorder used in conjunction with an accurately calibrated hydraulic testing machine. The test specimens were hand straightened as carefully as possible from a radius of curvature of 9 in. The straining produced in the straightening operation and the slight departure from straightness unquestionably had some effect upon the stress-strain curves.

MICROSTRUCTURE AND PREFERRED ORIENTATION

The existence of a preferred orientation was apparent in the microstructures for final anneals at 150° and 1250°F. and was particularly so for all final anneals that followed reductions of 74, 83.5 and 89.5 per cent. The preferred orientation,

bands in one, two or three sets (Fig. 2*a*). There are also some grains with no twinned portions at the surface of examination. There may be a number of mutually parallel bands in each set of twins. When two or three such sets occur within a grain, they either intersect or lie substantially at angles of 60° and 120° with each other. For such a case, it becomes apparent that crystallographic planes of the form {111} lie in the surface of the transverse section and that, therefore, the wire axis is parallel to the [111] direction. This, of course, follows from the fact that the twin boundaries may be considered as traces of {111} planes and that traces of three sets of {111} planes intersect at 60° and 120° only in the fourth {111} plane. The [111] axis is in agreement with that reported in the literature.¹

In axial sections, the preferredness 160° , to the wire axis or direction of reveals itself by a preponderance of grains drawing (Fig. 2*b*).

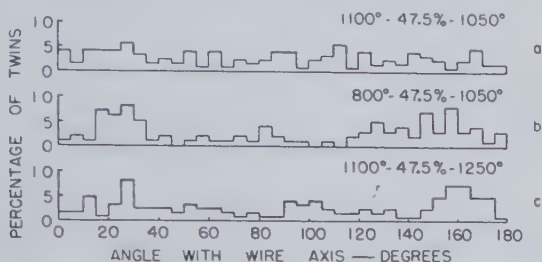


FIG. 3.—FREQUENCY DISTRIBUTION OF ANGLES OF TWIN BANDS ON AXIAL SECTIONS WITH RESPECT TO WIRE AXIS FOR SOME ANNEALED WIRES PREVIOUSLY COLD-DRAWN 47.5 PER CENT.

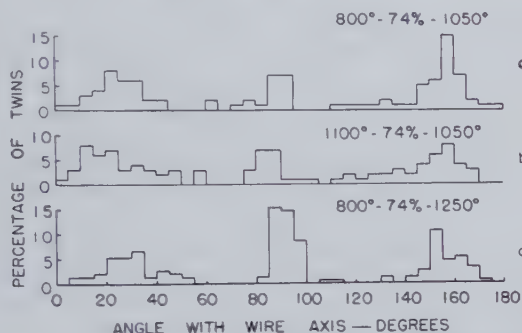


FIG. 4.—FREQUENCY DISTRIBUTION OF ANGLES OF TWIN BANDS ON AXIAL SECTIONS WITH RESPECT TO WIRE AXIS FOR SOME ANNEALED WIRES PREVIOUSLY COLD-DRAWN 74 PER CENT.

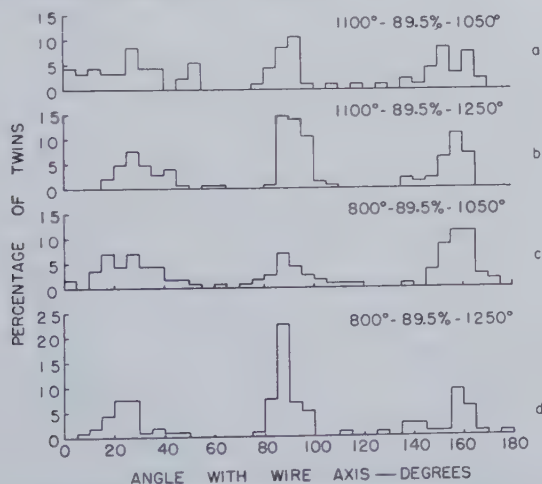


FIG. 5.—FREQUENCY DISTRIBUTION OF ANGLES OF TWIN BANDS ON AXIAL SECTIONS WITH RESPECT TO WIRE AXIS FOR SOME ANNEALED WIRES PREVIOUSLY DRAWN 89.5 PER CENT.

containing twins substantially at 90° and at two supplementary angles or ranges of angles, 20° to 30° and 150° to

One of the wires, finished according to the schedule, 800° —89.5 per cent— 1250° , and exhibiting very strongly pre-

ferred orientation, was subjected to X-ray analysis after being etched from the initial diameter, 0.132 in., to diameters of 0.130, 0.093, 0.065 and 0.032 in. The main

factors of working and annealing upon the occurrence of the preferred orientation.

Fig. 3a is for material finished by the schedule, 1100°—47.5 per cent—1050°,

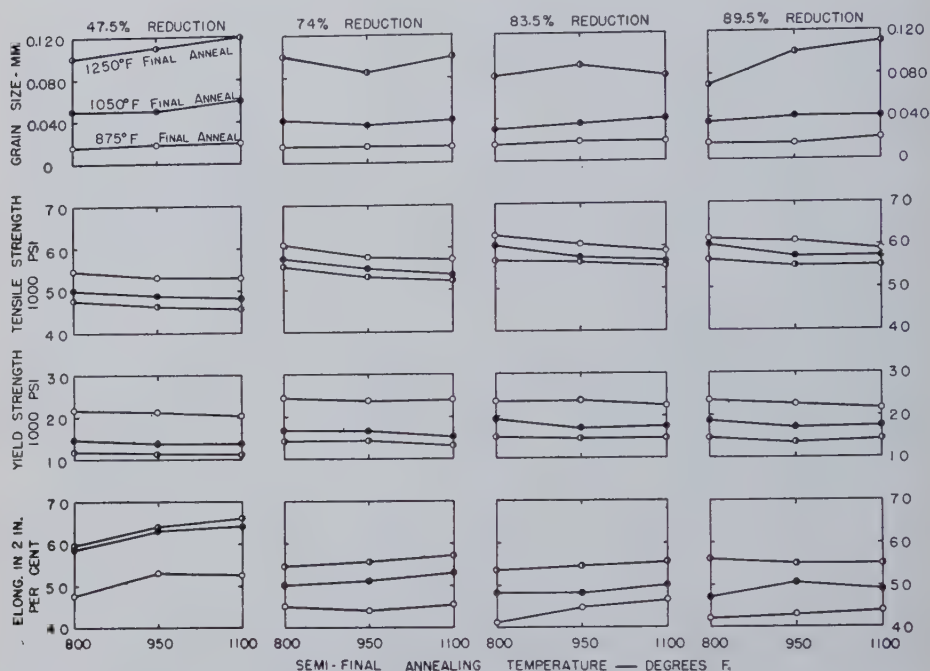


FIG. 6.—PROPERTIES OF 70-30 BRASS WIRE OF 0.132-INCH DIAMETER AS FINALLY ANNEALED AT 875°, 1050° AND 1250°F., AFTER HAVING BEEN COLD-DRAWN 47.5, 74, 83.5 AND 89.5 PER CENT FOLLOWING SEMIFINAL ANNEALS AT 800°, 950° AND 1100°F.

fiber axis was found to be [111] and there was a secondary axis of [100], these results thus being in agreement with the literature.¹ The [100] fibering was not visible in the outermost part of the wire; i.e., diameter of 0.130 in., but was present in all other positions. This secondary [100] texture is not particularly evident in the microstructure.

FREQUENCY DISTRIBUTION OF TWINS

Figs. 3, 4 and 5 show the frequency distribution of twin-band angles with respect to the wire axis as determined from photomicrographs of axial sections of several representative materials. They are sufficient to illustrate the effect of the

and indicates a substantially random orientation, there being no pronounced major peaks or troughs in the diagram. The distribution is produced by the moderate final working and the semifinal anneal, which is high with respect to the final anneal. Some preferredness appears in Fig. 3b, showing the effect of having the temperature of the semifinal anneal, 800°F., lower than the final anneal, 1050°F. It is only in the semifinal anneal that the processing of this item differs from that of Fig. 3a. Figure 3c also shows some preferredness and is for material that differs from that of Fig. 3a only in temperature of final anneal, 1250°F. The effect is similar to that in Fig. 3b.

Greater preferredness is shown in Fig. 4a, which is for wire finished by the schedule, 800°—74 per cent—1050°, and demonstrates the effect of the greater

anneal increases. It is probable that a state of random orientation cannot exist in any annealed condition that follows a reduction by drawing of 74 per cent or

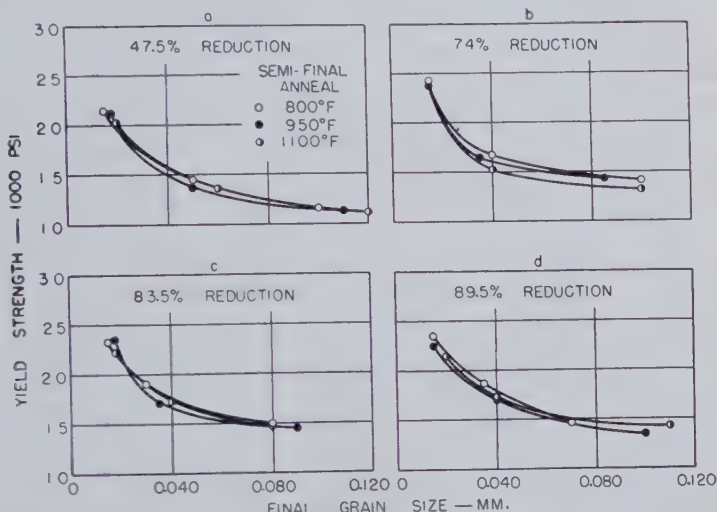


FIG. 7.—YIELD STRENGTH-GRAIN SIZE RELATIONSHIP FOR ANNEALED 70-30 BRASS WIRE OF 0.132-INCH DIAMETER AS AFFECTED BY THE PRECEDING COLD-DRAWING AND ANNEALING.

reduction, 74 per cent, in producing the preferredness (cf. Fig. 3b). Fig. 4b for the schedule, 1100°—74 per cent—1050°, shows only slightly less preferredness than does Fig. 4a and indicates the strong tendency toward preferredness for reductions of this magnitude, 74 per cent. Very strong preferredness, greater than in Fig. 4a, is apparent in Fig. 4c, this being the result of having a higher final annealing temperature than in Fig. 4a.

There is strong preferredness in Fig. 5a for the finishing schedule, 1100°—89.5 per cent—1050°, but hardly more so than in Fig. 4b. Preferredness increases in Fig. 5b, corresponding to the higher final annealing temperature, 1250°F. A similar effect of final anneal is to be noted in Figs. 5c and d.

The plots thus reveal the importance of the factors that control grain orientation. The degree of preferredness increases as the final annealing temperature increases and also as the reduction before the final

more. The temperature of the semifinal anneal is of lesser importance, but there is some indication that the degree of the preferredness in the finally annealed wire decreases as the temperature of the semifinal anneal increases. The factors influencing preferred orientation of grains in the annealed wire may therefore be considered to function qualitatively the same as for annealed brass strip.^{3,4} It is, of course, quite possible to produce a state of random orientation merely by employing a moderate final reduction, a moderate or low final annealing temperature, and a semi-final annealing temperature equal to or, preferably, higher than that of the final anneal.

The three pronounced peaks in the frequency distribution plots for the wires with strongly preferred orientation and the uniformity of the microstructure* from

* "Uniformity of microstructure" means that the angular distribution of the twin bands in the microstructure from edge to edge of the full axial section appears uniform to the eye.

edge to edge in the corresponding axial sections might suggest the possibility of a preferred axial or radial plane. This would place another restraint upon the preferredness of the wire beyond that

then rise abruptly at 90° . This condition apparently represents the true state of affairs, so that the preferred orientation of the annealed wire may be given only by the fiber axis designation.

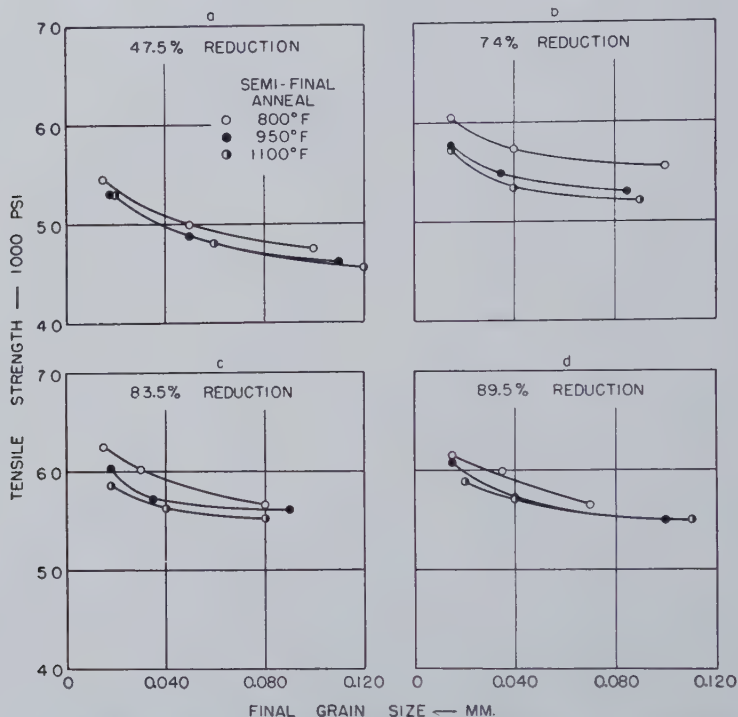


FIG. 8.—TENSILE STRENGTH-GRAIN SIZE RELATIONSHIP FOR ANNEALED 70-30 BRASS WIRE OF 0.132-INCH DIAMETER AS AFFECTED BY THE PRECEDING COLD-DRAWING AND ANNEALING.

included in the designation of a $[111]$ direction as the fiber axis. There is, indeed, one such plane, $\{112\}$, which could satisfy the observed conditions. If this plane were radially disposed, the twin bands on an axial plane would lie at 90° and at about 22° and 158° to the wire axis. However, the fact remains that, for random orientation of the grains about a perfectly aligned $[111]$ fiber axis, there would be concentrations of twins on any axial plane at about 20° and 160° to the wire axis in addition to that at 90° . There would be none in the intervals 0° – 20° and 160° – 180° . The concentrations would decrease considerably as the angles moved toward 90° and would

PROPERTIES OF ANNEALED WIRE

The properties obtained on the wire as subjected to the semifinal anneals require little comment other than to note the uniformity among the diameters with respect to grain size and tensile strength. These anneals at 800° , 950° , and 1100°F . resulted in grain-size ranges of 0.010 to 0.012 mm., 0.030 to 0.035 mm., and 0.060 to 0.070 mm., respectively, and corresponding tensile-strength ranges of 55,000 to 57,500 lb. per sq. in., 51,000 to 52,000 and 48,000 to 50,000 lb. per sq. inch.

Fig. 6, in which the grain size and tensile properties of the finally annealed

wire are plotted as functions of semifinal annealing temperatures, is a convenient means of representing the results of the tests upon the finished wire. The normally

regard to tensile strength, and the tensile strength-grain size curves for previous reductions of 74, 83.5 and 89.5 per cent are displaced upward to strength values

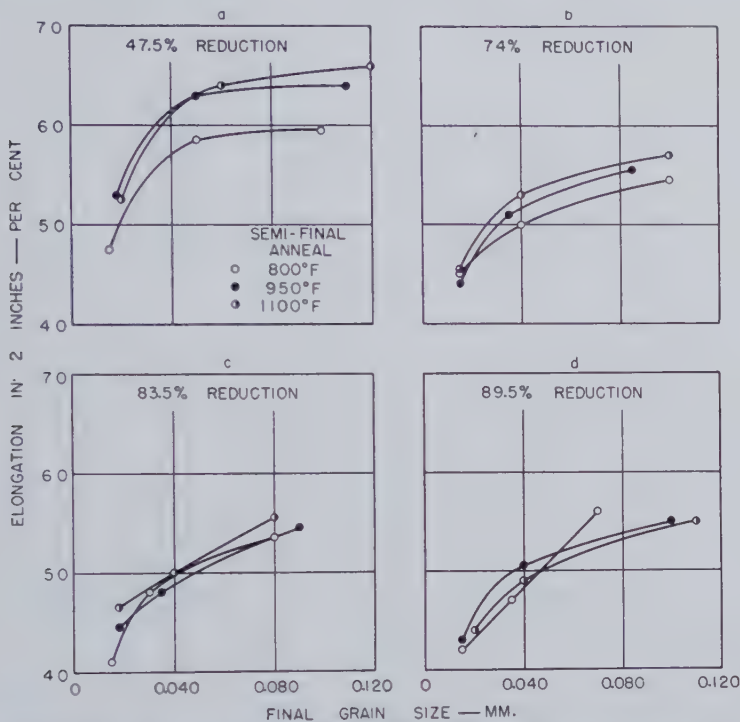


FIG. 9.—ELONGATION-GRAIN SIZE RELATIONSHIPS FOR ANNEALED 70-30 BRASS WIRE OF 0.132-INCH DIAMETER AS AFFECTED BY THE PRECEDING COLD-DRAWING AND ANNEALING.

expected effects of temperature on grain size, strength and elongation are evident in this figure, and, in addition, there are superimposed the effects of preferred orientation in a less obvious manner. These latter effects become more readily apparent when the various tensile properties are plotted as functions of grain size, as has been done in Figs. 7, 8 and 9.

Fig. 7 shows that the yield strengths (stress at 0.5 per cent elongation) of the wires drawn to the final size with the heaviest reductions, particularly 83.5 and 89.5 per cent, are materially higher than for the wire for which a 47.5 per cent reduction was used in the final draw. Fig. 8 shows a similar relationship with

about 15 to 20 per cent higher than for wire drawn 47.5 per cent before the final anneal. There is another definite trend within the group of curves shown for each reduction. This is an increase of strength for a given grain size as the semifinal annealing temperature decreases. It is first evident for the material of 47.5 per cent reduction, in which the wire given a semifinal anneal at 800°F. is slightly stronger than that semifinally annealed at 950° and 1100°F.

It is apparent that these yield and tensile-strength relationships with respect to grain-size parallel the occurrence of the preferred orientation, the controlling factors of which have been described above.

Strength increases as the intensity of the preferredness increases. This, of course, is to be expected from wire whose axis coincides with a preferred axis, [111],

afforded by Fig. 10, in which elongation is plotted as a function of tensile strength. These groups of curves show that the combination of strength and elongation over a

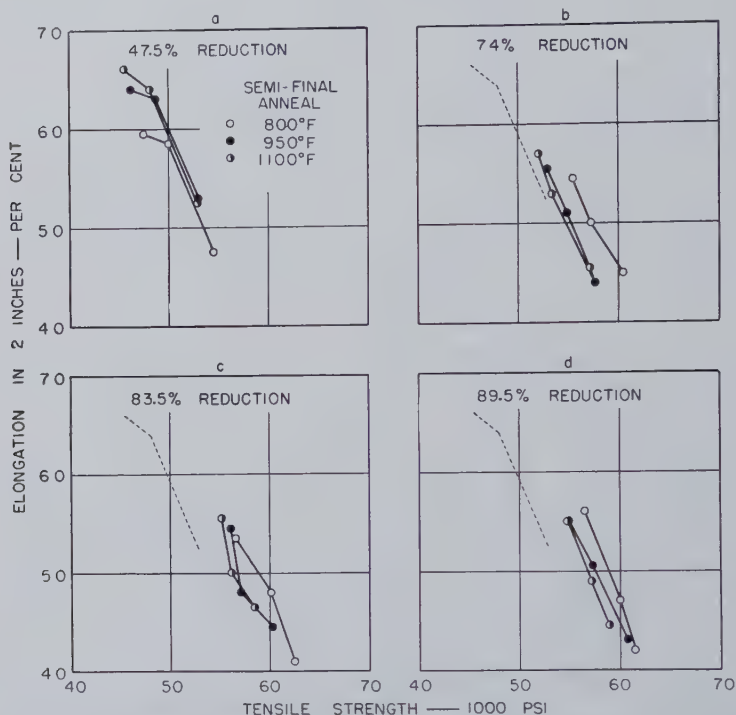


FIG. 10.—ELONGATION-TENSILE STRENGTH RELATIONSHIPS FOR ANNEALED 70-30 BRASS WIRE OF 0.132-INCH DIAMETER AS AFFECTED BY THE PRECEDING COLD-DRAWING AND ANNEALING.

Dotted line in *b*, *c* and *d* represents curve for annealed wire, previously annealed at 1100°F. and drawn 47.5 per cent as shown in *a*.

for it is known⁵ that yield strength of single crystals of alpha brass and of other face-centered cubic metals and alloys is maximum when the specimen axis is in the [111] direction.

Fig. 9 shows that elongation in the tension test is of the order of 10 per cent less for a given grain size for the conditions producing preferred orientation than for those producing the more random orientations. This is what might be expected qualitatively from the strength-grain size trends. A better comparison of the relationships between tensile strength and elongation for the various conditions is

limited range of elongation is better for the materials previously drawn 74, 83.5 and 89.5 per cent than for those drawn 47.5 per cent; that is, the strength corresponding to a given value of elongation is higher in this range. However, the high ductility of the more randomly oriented materials, those drawn 47.5 per cent before finally annealing, apparently cannot be attained by the materials with the strongly preferred orientation.

Values of modulus of elasticity were derived from the stress-strain curves made in the testing of the material and were found to be generally higher for final reductions

of 74, 83.5 and 89.5 per cent than for 47.5 per cent. These values are not included here because they were not quantitatively precise or consistent. This was undoubtedly because the stress-strain determinations were made on material that was hand straightened after annealing. The operation affected most of all the initial slope of the stress-strain curve from which the modulus

modulus of single-crystal specimens of face-centered cubic metals and alloys, including alpha brass, whose axes approach [111], is higher than for other orientations.⁶

SUMMARY

The effects of a number of cold-working and annealing conditions upon the occur-

TABLE 1.—*Tensile Properties of Some 70-30 Brass Wire as Drawn 10 Per Cent from 0.132 to 0.125 Inches and Mechanically Straightened*

Schedule to 0.132 In.			Modulus of Elasticity, Lb. per Sq. In.	Stress at 0.5 Per Cent Extension, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent
Semifinal Anneal, Deg. F.	Reduction, Per Cent	Final Anneal, Deg. F.				
1100	47.5	875	17,000,000	48,000	60,500	30
1100	47.5	1050	18,000,000	42,500	56,000	36
1100	47.5	1250	19,000,000	39,500	53,300	38
800	89.5	875	20,000,000	54,500	69,500	22
800	89.5	1050	22,500,000	54,000	67,800	25
800	89.5	1250	23,000,000	49,500	61,000	32

was calculated. The point of incidence of plastic deformation was also affected by the straightening operation, although the arbitrary yield strength, the stress at 0.5 per cent elongation, was affected but little and the tensile strength not at all. It was for this reason that the tests reported in Table 1 were made. These tests were on wires drawn 10 per cent and mechanically straightened, selected to represent the extreme processing conditions of the investigation, so that the most nearly random and the most strongly preferred orientations were represented. The stress-strain curves were much more nearly linear in the early stages than in the tests on the annealed materials, and were entirely consistent. The trends for the modulus values are the same as before, but the actual range of values is narrower, the highest value being 23,000,000 and the lowest value 17,000,000 lb. per sq. in. The increased values for modulus of elasticity for the particular preferred orientation is to be expected, for it is known that the

rence of preferred grain orientation in annealed 70-30 brass wire have been investigated. The preferred orientation, which may be designated most simply by the fiber axis, [111], decreases in intensity as the semifinal annealing temperature increases, but increases in intensity as the severity of the final reduction by drawing increases and also as the final annealing temperature increases. The converse of each of the factors as stated is to be inferred and it is to be noted that the last two factors, final draw and final anneal, are the most important in determining the degree of preferredness.

The preferred orientation is accompanied by significant increases in yield strength, tensile strength and modulus of elasticity over the values obtaining in randomly oriented wire of similar grain size.

ACKNOWLEDGMENTS

The authors wish to make due acknowledgment to Dr. D. K. Crampton for

his interest in the work, to Lt. Col. H. P. Croft for suggesting that the investigation be conducted, to Mr. F. P. Strieter, who performed much of the earlier experimental work, and to Dr. S. E. Maddigan and Mr. B. R. Zimmerman, who made the X-ray analysis reported in the paper. Thanks are also due to the Chase Brass and Copper Co. for permission to publish the results.

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DISCUSSION

(Alan Morris presiding)

G. EDMUNDS,* Palmerton, Pa.—Figs. 3, 4, and 5 represent the frequency of occurrence of twin bands as a function of their angle with the wire axis and are plotted over a range of 180° . Since supplementary angles are, for the purpose of this analysis, equivalent, the graphs should be symmetrical about the 90° point. If the data were plotted over an angular range of 90° , the number of data for each cell would be doubled.

H. L. BURGHOFF (author's reply).—Mr. Edmunds' statement with regard to the symmetry of the supplementary angles about the 90° point in Figs. 3, 4 and 5 is correct. However, not all of the possible sets of twin bands were present in a large part of the grains examined, and it was for this reason that the frequency distribution plots were made from 0° to 180° .

* Research Division, New Jersey Zinc Company (of Pa.).

Structure of Copper-zinc Alloys Oxidized at Elevated Temperatures

By F. N. RHINES,* MEMBER, AND B. J. NELSON,† JUNIOR MEMBER A.I.M.E.

(Chicago Meeting, October 1943)

STUDIES upon the rates of oxidation of copper alloys containing small quantities of the alloying elements^{1,2} have shown that steady growth of the scales at predictable rates is limited to a small concentration range and to oxidation at temperatures above 600°C., whereas unpredictable and erratic oxidation behavior is found with alloys containing larger additions and at low temperatures. The latter effect appears to be associated with modifications in the geometric disposition of the oxides.

At low concentrations of the baser elements in copper, simple oxidation behavior is typified by the formation of two distinguishable zones of oxidation: (1) a subscale composed of discrete particles of the oxide of the alloying element embedded in substantially pure copper and (2) an external scale composed of cuprous oxide (with a very thin layer of cupric oxide on the outside) containing particles of the alloying element distributed throughout, but most profusely near the metal surface (see Fig. 2, top). Where this type of structure obtains, the process of oxidation is believed to be implemented, and its rate controlled, by the diffusion of the reacting elements through a continuous matrix phase; i.e., through the alpha (metallic) phase of the

subscale and alloy and through the cuprous oxide of the external scale. Copper is presumed to diffuse outward through the cuprous oxide layer to the external surface, where it reacts to form more cuprous oxide.³ Oxygen is delivered at the oxide-metal interface in the form of cuprous oxide, which may either react with the alloying element to deposit its oxide at the inner limit of the external scale or dissolve in the pure copper that remains at the surface of the metal after it has become depleted in its oxidizable alloying elements. Both oxygen and the alloying element are pictured as diffusing through the metal, the oxygen inward and the alloying element outward. Where the two diffusion streams meet in sufficient concentration the oxide of the subscale is precipitated. If the oxygen pressure in the surrounding atmosphere is just below the pressure necessary to maintain cuprous oxide undecomposed, no cuprous oxide can be formed; some of the oxide of the alloying element may form upon the external surface, if its decomposition pressure is below that of cuprous oxide, and a normal subscale appears. This condition is achieved experimentally by enclosing the alloy with cuprous oxide together with an excess of copper.

At temperatures from 600°C. downward, the precipitated oxides tend to accumulate at the grain boundaries of the alpha phase where a relatively small volume establishes a partial barrier to the diffusion of the reactants. Similarly, large volumes of precipitated oxides tend to deposit in various patterns that may be expected to

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* Assistant Professor of Metallurgy and Member of the Staff, Metals Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa.

† Research Assistant, Metals Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa.

¹ References are at the end of the paper.

hinder the diffusion of the reactants in the alpha phase. The rate of oxidation thus becomes subject to the influences of the geometry of the paths among the foreign oxide particles, the changes in form that these particles and the paths between them suffer with the passage of time at high temperatures, and, perhaps, to the rates of diffusion within the foreign oxide.

For this reason, a knowledge of the structure of the oxide deposited in the scale layers formed upon the less dilute alloys is prerequisite to an understanding of their modes and rates of oxidation. By way of an approach to such a study, the structures developed upon the oxidation of the alloys of the copper-zinc system have been examined and are here described. The survey, including some observations from previous investigations, covers the concentration range of 10 to 98 per cent of zinc and a temperature range of 300° to 900°C.

EXPERIMENTAL PROCEDURE

The method of experimentation, previously described in some detail,¹ was, briefly, as follows: Alloys prepared by melting OFHC copper and electrolytic zinc under borax in clay-graphite crucibles in a gas furnace were chill-cast as ingots 1 by 2 by 12 in. The cast surfaces were scalped and, wherever possible, the bars were reduced 75 per cent by cold-rolling. Samples 1/2 by 1/2 by 1/4 in. were then cut from the rolled plates or cast bars and were smoothed on 000 emery paper. Two kinds of oxidation treatments were applied: (1) heating with free access to the air and (2) heating in a closed iron chamber packed with a mixture of cuprous oxide and copper metal powder or foil. In all cases an electrically controlled ($\pm 5^\circ\text{C}.$) muffle furnace was employed. When necessary to preserve the scale intact, the specimens, heated in the air, were immersed in Woods metal before they had cooled much below the heat-treating temperature. All samples

were cross-sectioned, polished, etched,* and examined by conventional metallographic techniques. The alloys were analyzed for their copper content and the residue was assumed to be zinc; a list of the alloys, together with their analyses and oxidation treatments, is given in Table 1.

OBSERVATIONS

The chief structural characteristics of the oxidized alloys are portrayed by the synthetic drawings of Fig. 1a and 1b and by the photomicrographic series of Figs. 2 to 9b, inclusive. An average impression of the structures observed in all of the samples listed in Table 1 at all points along the surface of each is represented by the drawings. In order to indicate more clearly the sequence of changes in oxidation behavior associated with composition change, the liberty of interpolating between the alloy compositions examined has been taken. The fine details of the structures are best seen in the photographs, which have been so selected as to be representative within the temperature and concentration ranges studied; the drawings, Fig. 1, will serve as a key for the identification of the constituents appearing in the photographs. A list of some of the systematic features of these structures may be of assistance in arriving at an understanding of the mechanism of oxidation.

1. *Cuprous Oxide in the Scale.*—Cuprous oxide appears as a constituent of the external scale with oxidation in the air at all temperatures in alloys containing up to about 20 per cent of zinc (Fig. 2). There is some variation from sample to sample in the apparent limit of the occurrence of cuprous oxide. At low zinc concentrations

* A single etch suitable for distinguishing the several metallic phases of the copper-zinc system without seriously obscuring the structure of the oxide was made by mixing equal parts of the following solutions:

(1) 10 grams of CrO_3 in 90 c.c. of water.
(2) 6 grams of $\text{K}_2\text{Cr}_2\text{O}_7$ + 24 c.c. of concentrated H_2SO_4 + 12 c.c. of saturated NaCl water solution + 300 c.c. of water.

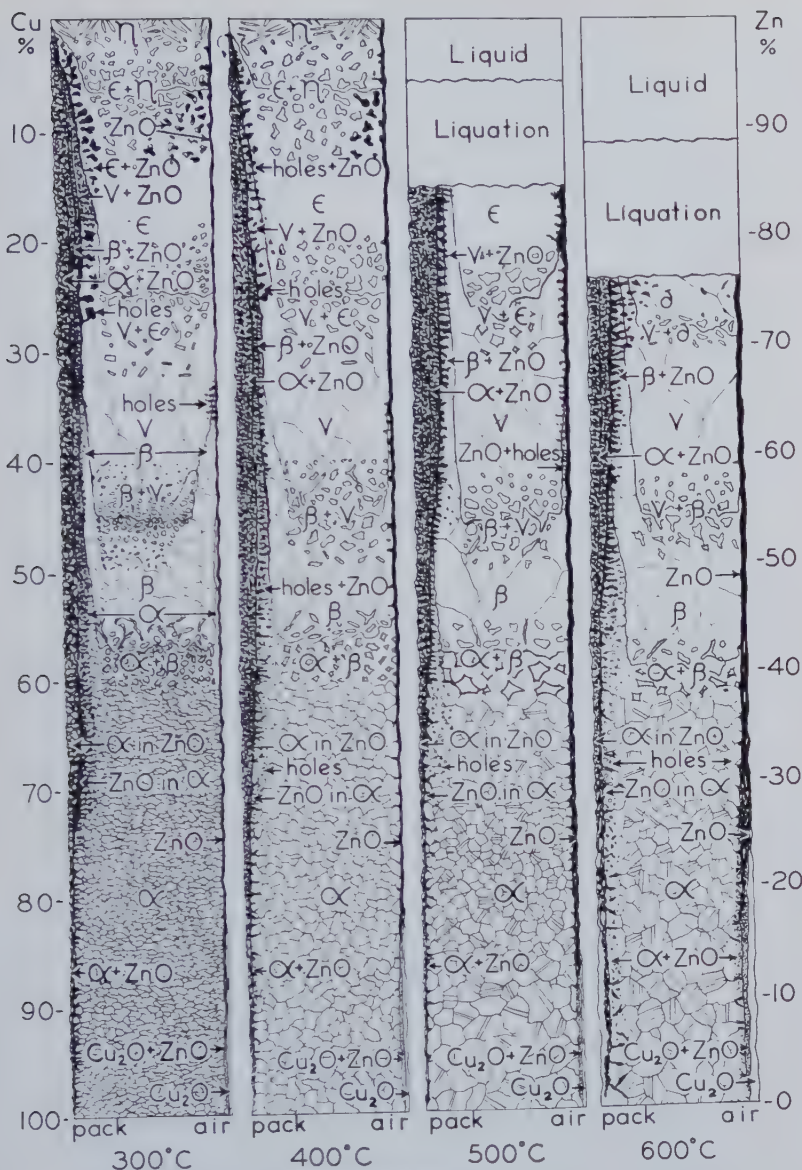


FIG. 1a.—SYNTHETIC DRAWING OF STRUCTURES SEEN IN COPPER-ZINC ALLOYS OXIDIZED AT 300°, 400°, 500° AND 600°C.

The center of each strip represents the structure of the unattacked alloys from pure zinc at the top to pure copper at the bottom. Structures produced by oxidation in the air are shown along the right-hand edge, those produced by oxidation in the cuprous oxide "pack" along the left-hand edge. No quantitative significance is to be attached to the depth of the oxidized zones.

the cuprous oxide is the matrix phase of the scale and contains embedded particles of zinc oxide in greatest concentration near the metal surface. As the zinc content of the

outside the zinc oxide and then as occasional particles. No cuprous oxide forms on the samples heated in the cuprous oxide "pack" (Fig. 3).

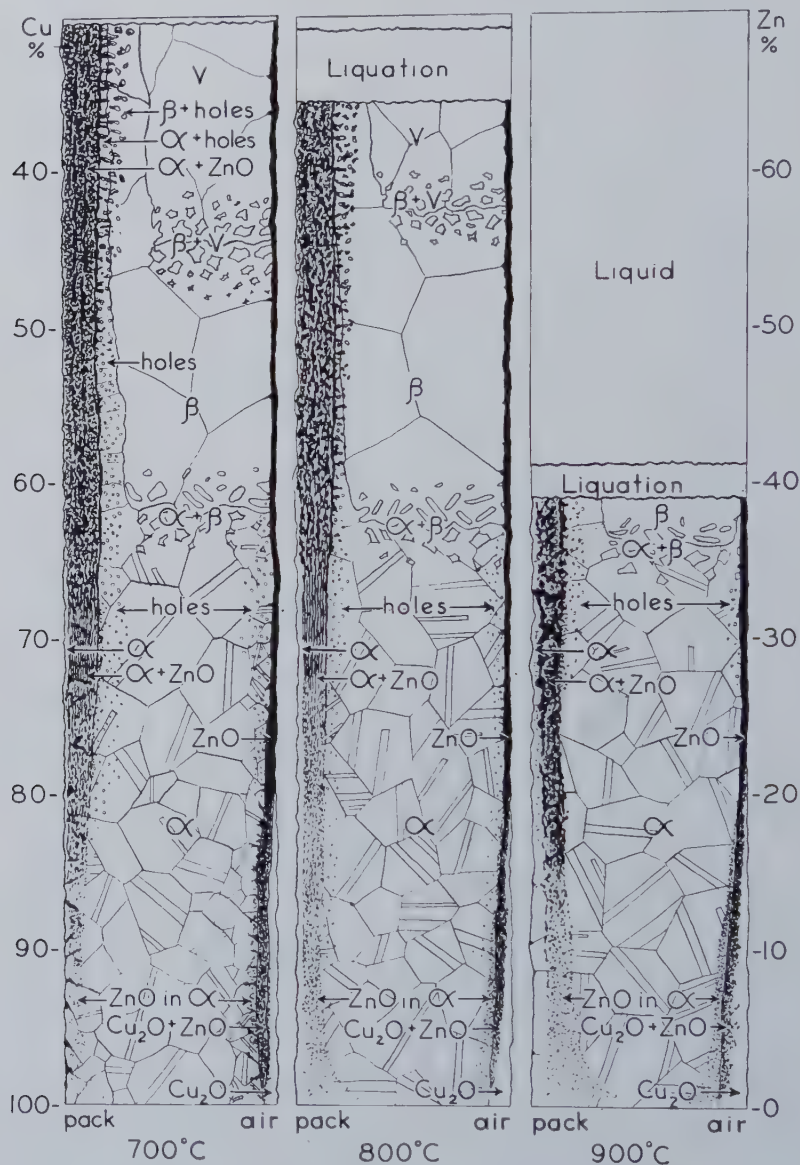


FIG. 1b.—SAME AS 1a, BUT OXIDIZED AT 700°, 800° AND 900°C.

alloy increases, the underlying zinc oxide phase gradually becomes continuous and the cuprous oxide appears first as a layer

2. *Zinc Oxide in the Scale.*—A continuous film of zinc oxide forms on alloys containing 20 per cent and more of zinc when oxidized

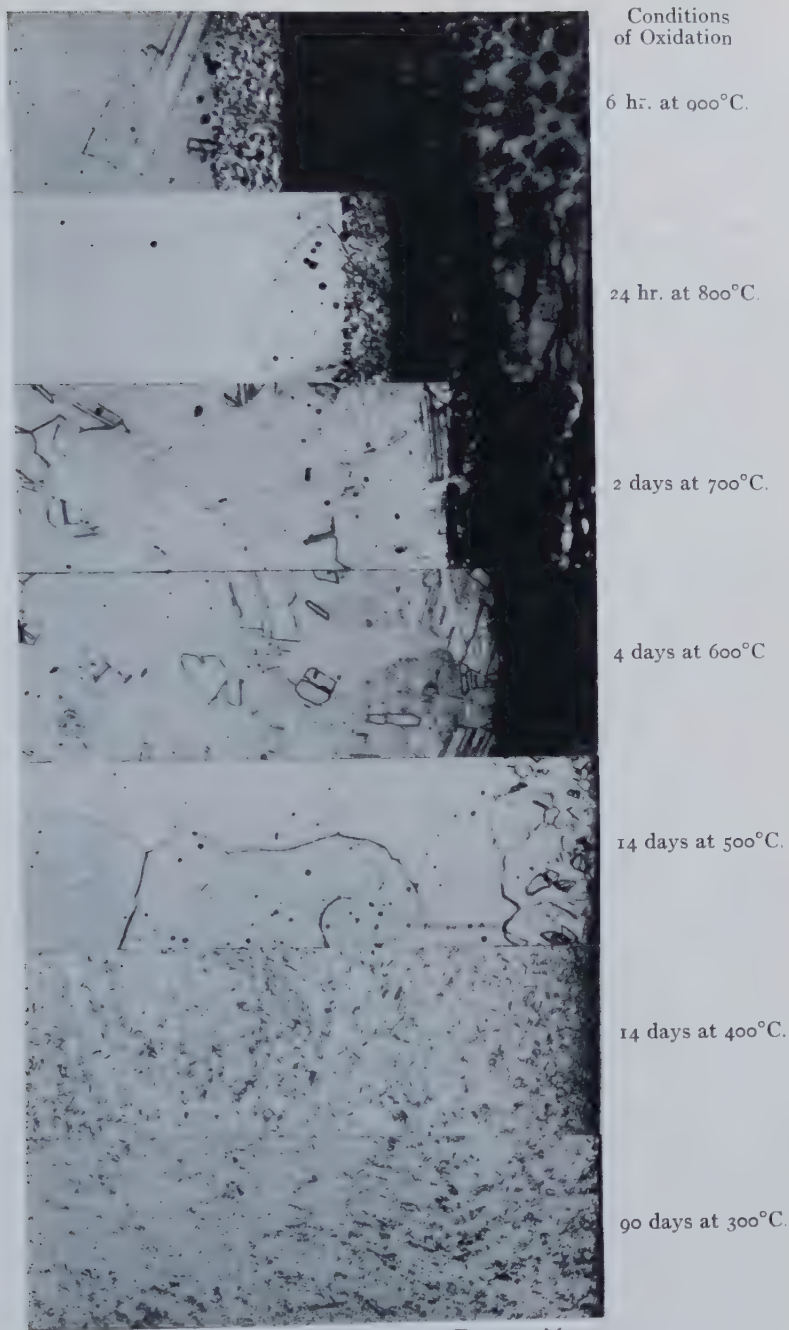


FIG. 2.—ALLOY NO. 10 OXIDIZED IN AIR. ETCHED. $\times 100$.
External surface on the right-hand side.

Conditions
of Oxidation

6 hr. at 900°C.

24 hr. at 800°C.

2 days at 700°C.

4 days at 600°C.

14 days at 500°C.

14 days at 400°C.

90 days at 300°C.

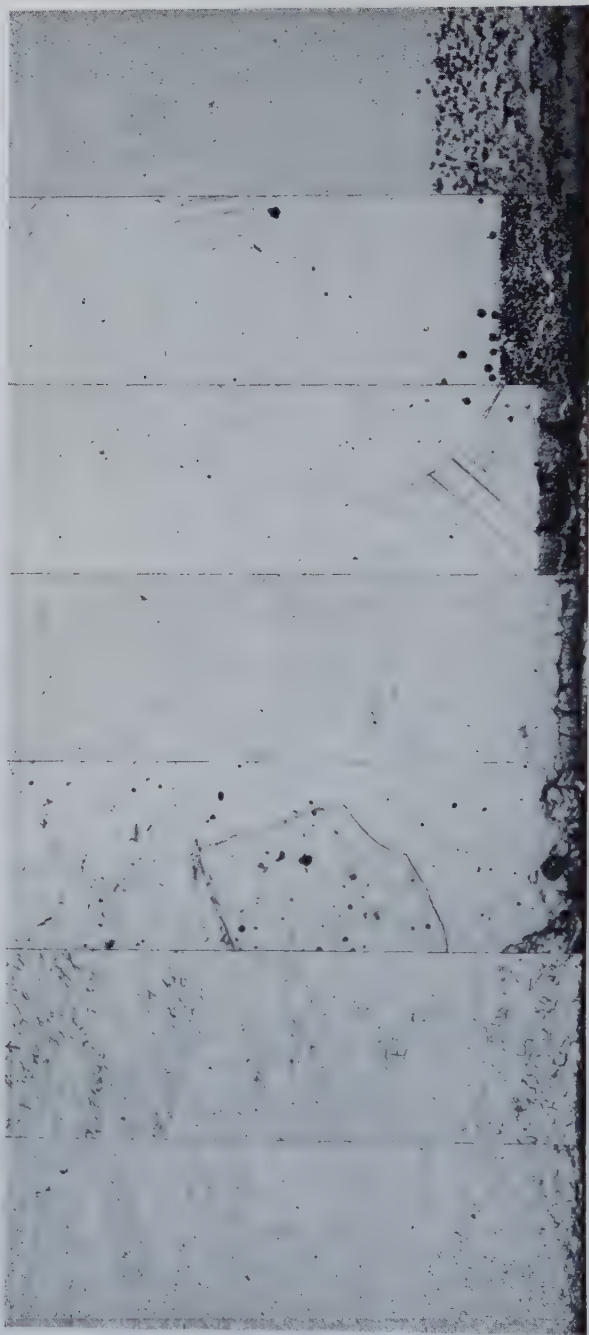


FIG. 3.—ALLOY NO. 10 OXIDIZED IN CUPROUS OXIDE "PACK." ETCHED. $\times 100$.
External surface on the right-hand side.

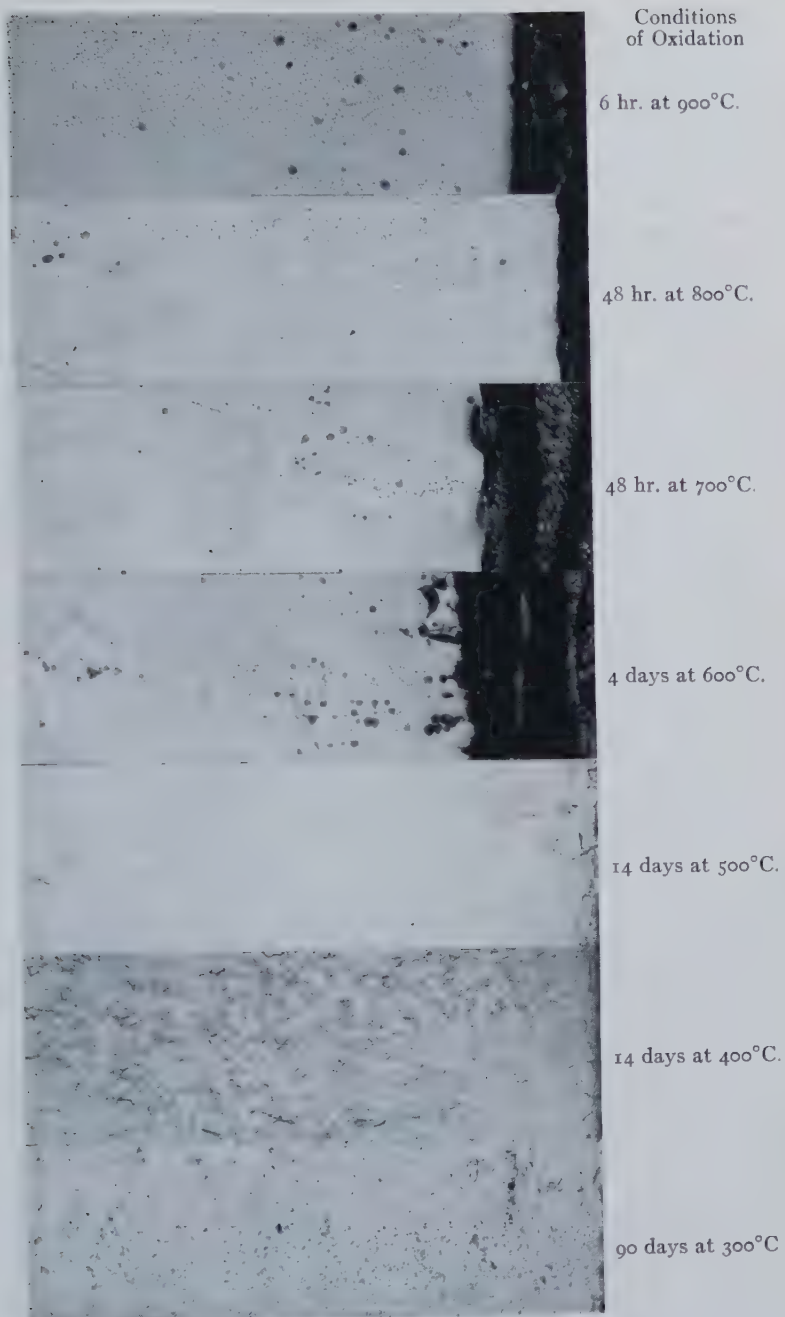


FIG. 4.—ALLOY NO. 30 OXIDIZED IN AIR. ETCHED. $\times 100$.
External surface on the right-hand side.

Conditions
of Oxidation

6 hr. at 900°C.

24 hr. at 800°C.

9 days at 700°C.

4 days at 600°C.

14 days at 500°C.

14 days at 400°C.

90 days at 300°C.



FIG. 5.—ALLOY NO. 30 OXIDIZED IN CUPROUS OXIDE "PACK." ETCHED. $\times 100$.
External surface on the right-hand side.

in the air (Fig. 10). The film is relatively thin, somewhat thicker at higher temperatures, and exhibits very little growth with the passage of time (its thickness is exaggerated in the drawings, Fig. 1). With very rare exceptions, the zinc oxide spalls away from the metal surface as the metal cools; sometimes the film is wrinkled. Probably this is the result of a large difference between the coefficients of expansion of the oxide and the metal. Where zinc oxide is associated with cuprous oxide, it has a pink tint, suggesting the presence of dissolved copper. This tint persists to some extent in the absence of cuprous oxide wherever the zinc oxide is in contact with the alpha (copper-rich) phase. Formed directly upon the beta phase, the tint changes to pale yellow and upon the gamma, epsilon and eta phases to a gray-white. These observations apply as well to the samples oxidized in "pack" as to those oxidized in the air. Froelich⁴ presents analyses of the scales formed upon brass that show a copper content of approximately 12 per cent in the mixed oxides occurring on an alloy containing 20 per cent of zinc and less than one per cent of copper in the "pink" zinc oxide from a 30 per cent zinc brass.

3. *Zinc Oxide in the Subscale.*—No continuous film of zinc oxide is found upon the external surfaces of samples oxidized in the cuprous oxide "pack." Zinc oxide does appear at (or at least very near) the outside, but in patches, not uninterrupted sheets. Usually some zinc oxide is found distributed through the cuprous oxide packing material. Since the vapor pressure of zinc oxide (presumed to be of the order of 1×10^{-10} mm. at $400^{\circ}\text{C}.$) is very much lower than that of zinc (1×10^{-1} mm. at $400^{\circ}\text{C}.$) it must be assumed that some zinc, arriving at the metal surface, vaporizes and later oxidizes as it comes into contact with cuprous oxide. The formation of a protective and durable film of zinc oxide upon alloys oxidized in the air further argues against a large evaporation of zinc

oxide as such. Thus the zinc oxide formed within the samples during "pack" oxidation may well be confined to that produced as oxygen is delivered to the zinc through a layer of copper; where the zinc reaches an external surface its rate of evaporation probably exceeds its rate of oxidation.

4. *Copper Rim on the Subscale.*—Samples oxidized in the cuprous oxide "pack" exhibit a layer of red copper at the outside surface (Figs. 3, 5, 7 and 9). Frequently this layer spalled away as the sample cooled, but some remnants of it were retained in almost all cases. Similar oxide-free zones have been observed at the surfaces of other oxidized alloys.^{1,5} It has been suggested that, during the early stages of the reaction, the alloying element is delivered to the surface more rapidly than oxygen; when the surface metal becomes sufficiently depleted in the alloying element its rate of diffusion outward falls below that of oxygen inward and a subscale is initiated somewhere beneath the surface where the combined concentrations of oxygen and the alloying element reach values favorable to the nucleation of the oxide. In the present case the zinc reaching the surface is presumably dissipated to a large extent by evaporation instead of being fixed as an external scale.

5. *Simple Subscales.*—Simple internal oxidation is confined to the copper-rich alloys and to high temperatures of reaction (Figs. 2 and 3). The particle size of the zinc oxide in the subscale increases as the zinc content of the alloy rises; at the same time the depth of the subscale decreases somewhat. Beyond 18 per cent of zinc, no true subscale was found in samples heated in the air, but the subscale persisted in degenerate form almost to the maximum zinc concentrations in the samples treated in "pack."

6. *Liesegang Structures.*—At 10 per cent of zinc the oxide particles of the subscale exhibit a faint tendency to occur in rows (layers) parallel to the external surface,

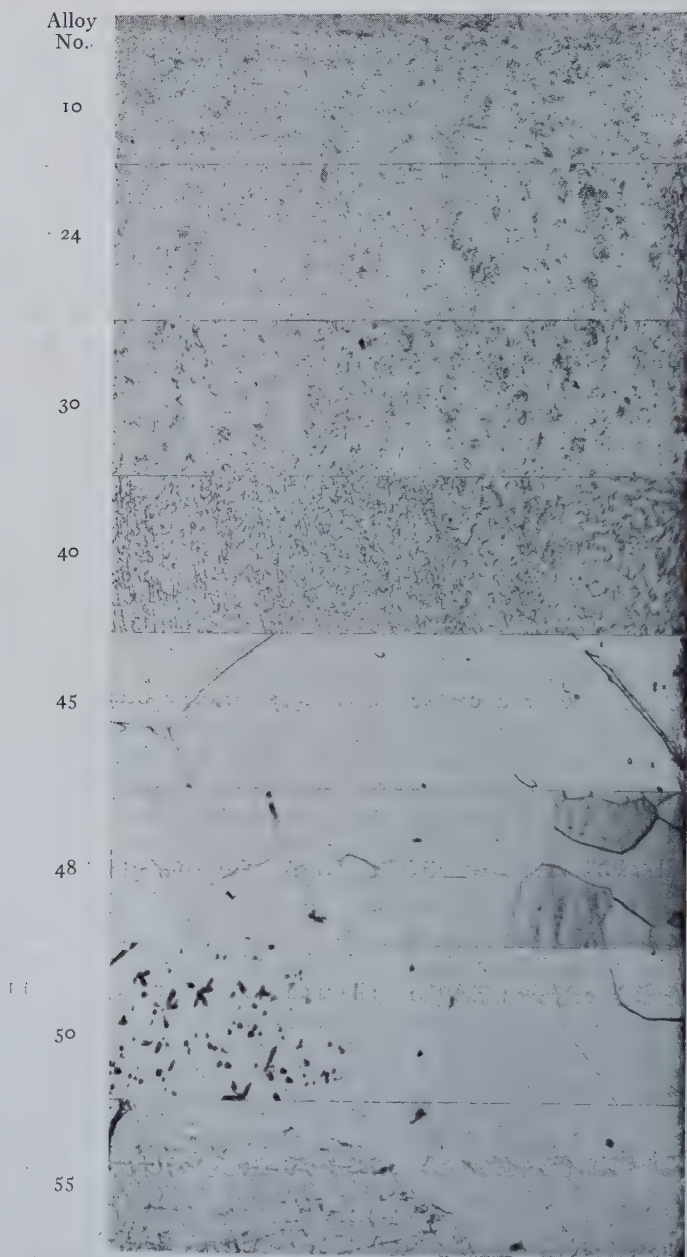


FIG. 6a.—SERIES OF COPPER-ZINC ALLOYS (10 TO 55 PER CENT ZINC) OXIDIZED IN AIR FOR 90 DAYS AT 300°C. ETCHED. $\times 100$.
External surface on the right-hand side.

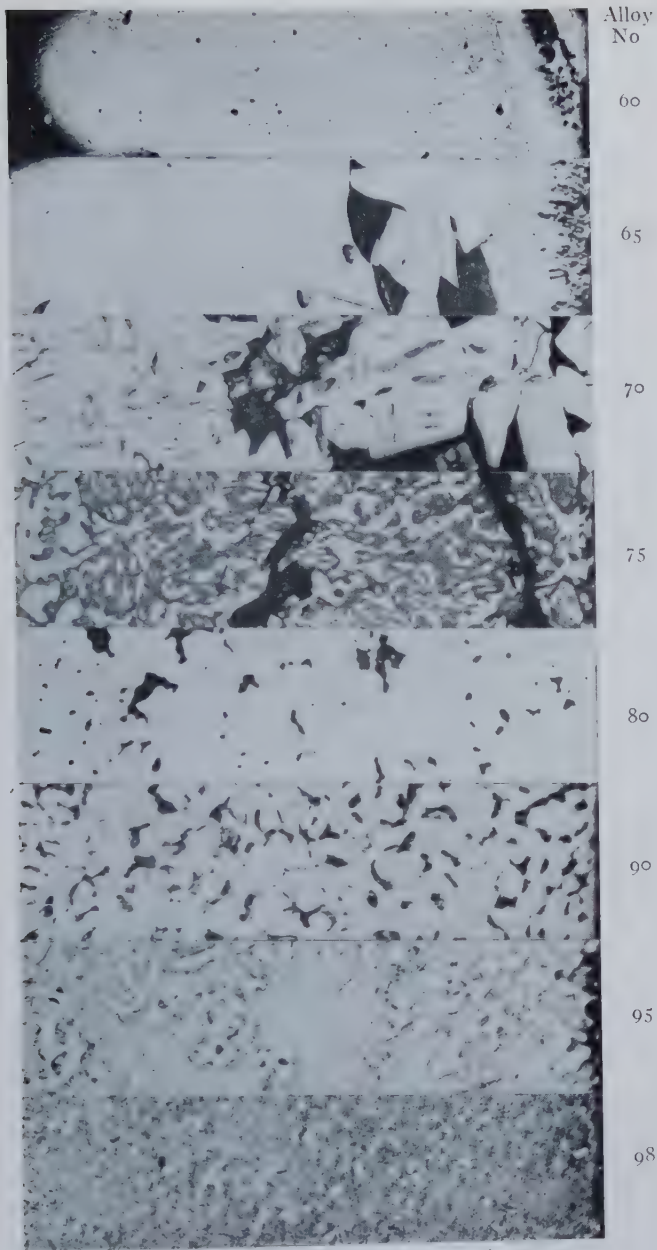


FIG. 6*b*.—SERIES OF COPPER-ZINC ALLOYS (60 TO 98 PER CENT ZINC) OXIDIZED IN AIR FOR 90 DAYS
AT 300°C. ETCHED. $\times 100$.
External surface on the right-hand side.

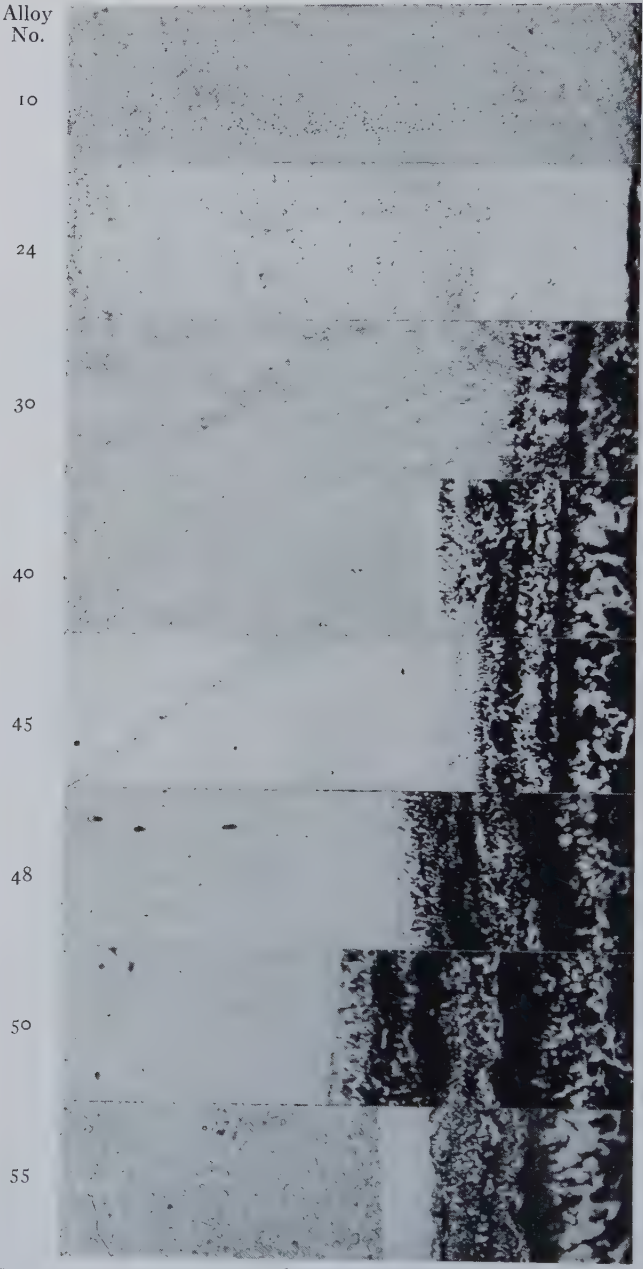


FIG. 7a.—SERIES OF COPPER-ZINC ALLOYS (10 TO 55 PER CENT ZINC) OXIDIZED IN CUPROUS OXIDE "PACK" FOR 90 DAYS AT 300°C. ETCHED. $\times 100$.
External surface on the right-hand side.



FIG. 7b.—SERIES OF COPPER-ZINC ALLOYS (60 TO 98 PER CENT ZINC) OXIDIZED IN CUPROUS OXIDE "PACK" FOR 90 DAYS AT 300°C . ETCHED. $\times 100$, EXCEPT ALLOY 90, WHICH IS $\times 60$. External surface on the right-hand side.

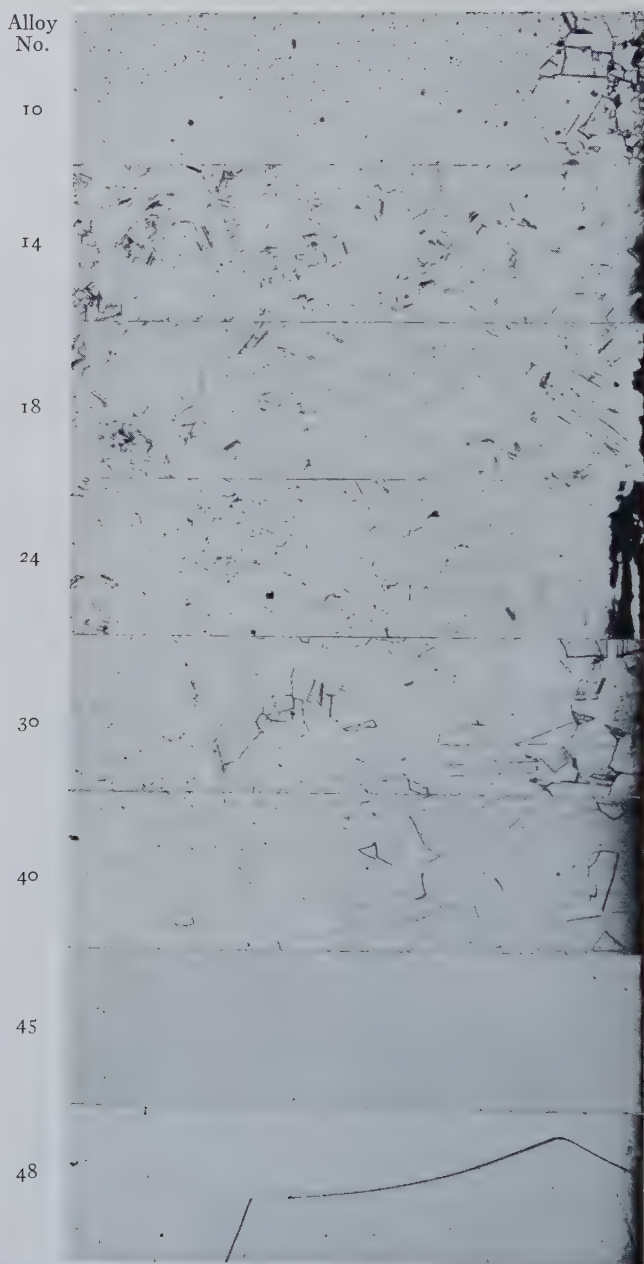


FIG. 8a.—SERIES OF COPPER-ZINC ALLOYS (10 TO 48 PER CENT ZINC) OXIDIZED IN AIR FOR 14 DAYS AT 500°C. ETCHED, $\times 100$.
External surface on the right-hand side.



FIG. 8b.—SERIES OF COPPER-ZINC ALLOYS (50 TO 90 PER CENT ZINC) OXIDIZED IN AIR FOR 14 DAYS AT 500°C. ALLOY 90 SHOWS LIQUATION. ETCHED. $\times 100$. External surface on the right-hand side.

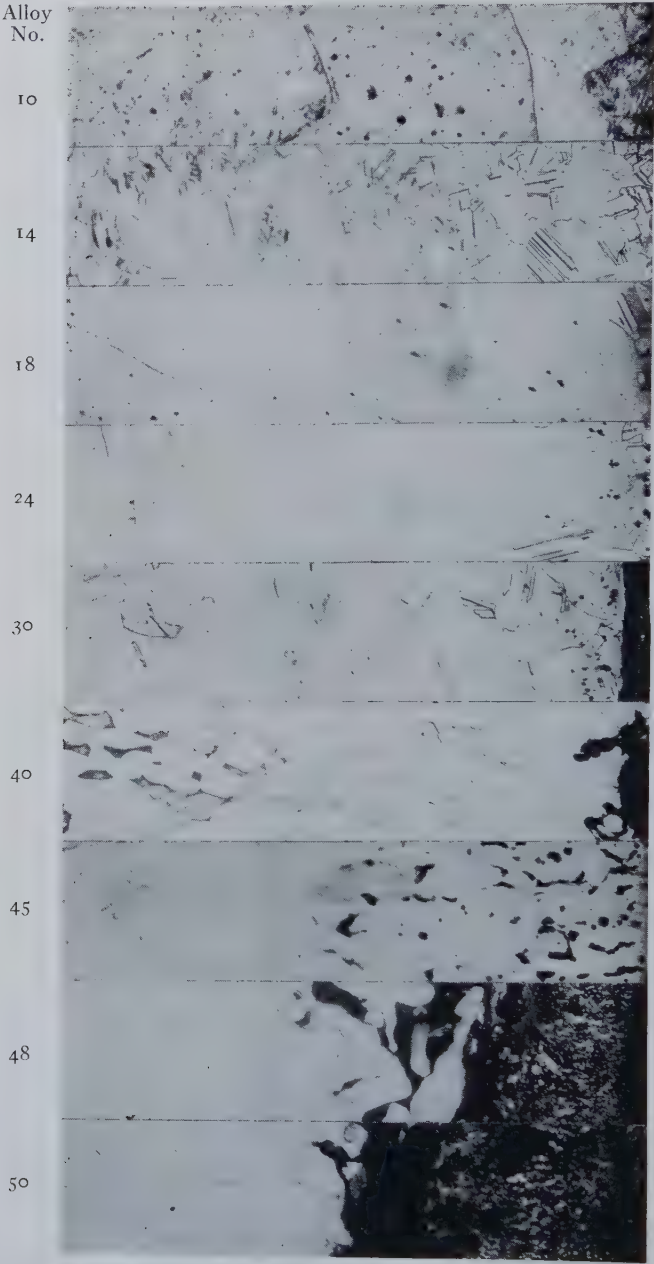


FIG. 9a.—SERIES OF COPPER-ZINC ALLOYS (10 TO 50 PER CENT ZINC) OXIDIZED IN CUPROUS OXIDE "PACK" FOR 14 DAYS AT 500°C. ETCHED. $\times 100$.
External surface on the right-hand side.



FIG. 9b.—SERIES OF COPPER-ZINC ALLOYS (55 TO 98 PER CENT ZINC) OXIDIZED IN CUPROUS OXIDE "PACK" FOR 14 DAYS AT 500°C. ALLOYS 90, 95, AND 98 SHOW LIQUATION. ETCHED. $\times 60$, EXCEPT ALLOY 95, WHICH IS $\times 100$.
External surface on the right-hand side.

Figs. 3 (900°C.) and 11. This tendency increases with rising zinc content, until, at 30 per cent of zinc, the oxide is laid down in almost continuous bands (layers) alter-



FIG. 10.—ALLOY NO. 30 OXIDIZED 9 DAYS AT 700°C. IN AIR. UNETCHED. $\times 100$.

Notice layer of zinc oxide, cracked away from metal surface and somewhat wrinkled, along lower edge of metal. The round spots within the metal are holes.

nately with red copper, Figs. 5 (700° and 800°C.) and 12. The analogy between this structure and the well-known Liesegang rings of colloid chemistry has been pointed out.¹ For convenience, this structure and others involving banding parallel to the surface will hereafter be referred to as Liesegang structures.

7. *Voids*.—At a zinc concentration of 30 per cent, cavities are found in the alpha phase to a considerable depth beyond the maximum penetration of oxidation in samples treated at all but the lowest temperatures (Figs. 4 and 5). Occasionally this effect is seen at zinc concentrations as low as 10 per cent. Apparently, the volume shrinkage necessary to compensate for the extraction of zinc is effected, in part at least, by the development of voids. It was not found possible, with the evidence at hand, to compare the volume of the holes with a calculated shrinkage. Where the

cavities occurred outside the zone of oxidation, they were obviously empty. Those within the zone of oxidation appeared to be partly or completely filled with zinc oxide. With increasing zinc content, the holes become larger and elongated, having a tendency to lie perpendicular to the outside surface (Figs. 6, 7, 8, 9, 13 and 14).

8. *Layers of the Metallic Phases with "Pack" Oxidation*.—In general, samples oxidized in "pack" exhibit a thick layer of the alpha phase mixed with zinc oxide at the outside of the scale followed by successive thinner layers of zinc oxide with the beta, gamma, epsilon (or delta) and eta phases toward the interior, up to that phase present in the original alloy. Sometimes oxidation fails to penetrate to the phase present in the core of the sample, but invariably extends into, if not through, the adjacent phase layer. For example, in alloy 75, at temperatures below 700°C., zinc oxide appears mixed with the alpha phase and extends part way through the beta phase, but does not extend into the gamma (Fig. 9b). Owing to the complexity of the oxide pattern, it was often difficult to identify intermediate phases within the scale. The beta layer becomes relatively thin in high-zinc alloys and may vanish except for occasional pockets between the alpha and gamma layers. Nevertheless, all expected layers were found in alloy 98 oxidized in "pack" at 300°C.

9. *Layers of the Metallic Phases with Air Oxidation*.—Corresponding layers of the metallic phases are generally absent with air oxidation. At 300°C. two metallic layers formed at some compositions, but at higher temperatures two phases were seen in the microstructures only as they appeared in normally two-phase alloys. The surface zinc oxide film formed directly upon each of the metallic phases of the polyphase system.

10. *Grain-boundary Precipitation*.—With decreasing temperature there is an increased tendency for zinc oxide to accumu-

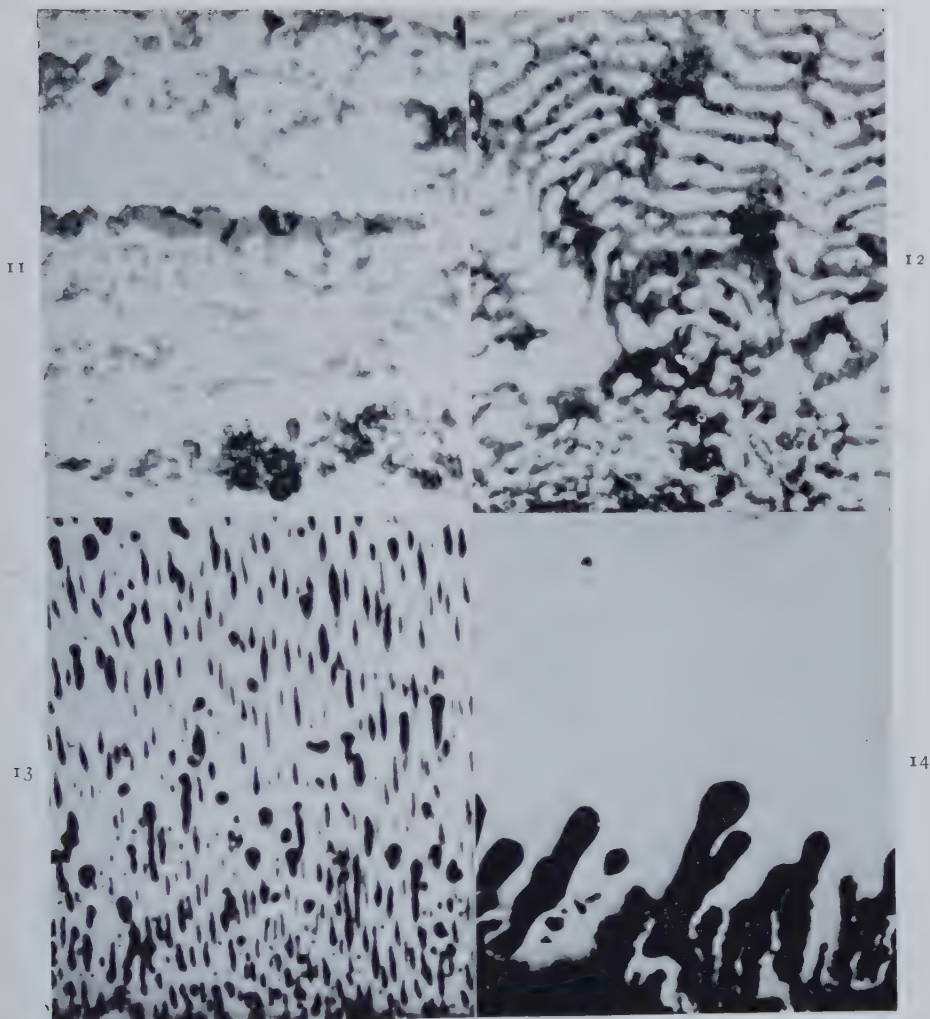


FIG. 11.—ALLOY NO. 10 OXIDIZED 12 HOURS AT 900°C . IN CUPROUS OXIDE "PACK." UNETCHED.
 $\times 500$.

Shows a tendency for the zinc oxide in the subscale to deposit in rows.
 FIG. 12.—ALLOY NO. 30 OXIDIZED 290 HOURS AT 800°C . IN CUPROUS OXIDE "PACK." UNETCHED.
 $\times 500$.

Shows a well developed Liesegang structure.
 FIG. 13.—ALLOY NO. 48 OXIDIZED 96 HOURS AT 700°C . IN CUPROUS OXIDE "PACK." UNETCHED.
 $\times 100$.

An unusually well developed pattern of cavities perpendicular to the outside surface. The scale has not been preserved.

FIG. 14.—ALLOY NO. 55 OXIDIZED 168 HOURS AT 600°C . IN CUPROUS OXIDE "PACK." UNETCHED.
 $\times 100$.

Typical cavities perpendicular to and connecting with the external surface. The scale has not been preserved.

late at grain boundaries in the metal matrix (Fig. 3). Definite grain-boundary precipitation first appears at about 700°C . and from 500°C . downward all of the oxide

transcrystalline streamers, roughly perpendicular to the surface, and resembling grain-boundary precipitation in some respects; the latter configuration is probably the result of the oxide accumulating within shrinkage cavities.

11. *Liesegang Structures in High-zinc Alloys.*—The "degenerate subscale" produced by the "pack" oxidation of alloys containing in excess of 40 per cent of zinc seems to have been formed by a combination of true precipitation of the oxide within the metal matrix and deposition within cavities (Fig. 15). In repeating layers, the oxide precipitation becomes heavier as in a Liesegang band, but the periods are much farther apart than in the normal Liesegang structure (Figs. 7 and 9). A possible reason for this is that oxygen diffusion is slowed by the interference of zinc oxide particles until the rate of delivery of zinc so exceeds that of oxygen that the oxide forms for a long period at one front and perhaps even ceases for a time. The process of oxidation can then be resumed only when the zinc oxide film is broken by mechanical rupture (spalling) or by spheroidization. The zinc oxide apparently becomes the continuous phase within the zones of its greatest concentration.

12. *Spalling.*—Spalling of the scales is common. Differential thermal contraction as a possible cause of this effect in samples oxidized in the air has been discussed. In the "pack" oxidized samples, the rupture usually follows one or several of the Liesegang layers of zinc oxide. Apparently spalling, under these circumstances, occurs spontaneously during oxidation and not first at the time of cooling from the heat-treating temperature. A number of high-zinc alloys were found to have separated into loose concentric shells during "pack" oxidation; when shaken the internal parts could be heard rattling and upon sectioning it was seen that the layers were too far separated to have parted owing to thermal shrinkage alone. (Samples 70, 75 and 80 of



FIG. 15.—ALLOY NO. 55 OXIDIZED 48 HOURS AT 800°C . IN CUPROUS OXIDE "PACK." UNETCHED. $\times 100$.

Shows the manner in which zinc oxide deposits within a matrix of copper in the high-zinc alloys. The wide crack between the metal and the scale contained remnants of zinc oxide not visible in the picture. Zinc oxide deposits resembling the pattern of holes at the top of the picture can be seen in the scale.

seems to be deposited in the grain boundaries. Where zinc oxide separates within the beta, gamma, epsilon and eta phases, it is sometimes seen segregated at the grain boundaries but more frequently forms

Fig. 9 show this effect, but the gap has been shortened in making the pictures.) Perhaps the zinc oxide depositing in cavities toward the outside continues to form after the holes are filled, expanding them and thus enlarging the subscale until it breaks away from the base metal along the plane of greatest weakness, where the oxide is present in the highest concentration. At low temperatures and low zinc concentrations spalling follows grain boundaries where the zinc oxide again is most concentrated. There is no evidence to show that rupture occurs before cooling in these cases.

13. *Strain Markings*.—Strain markings, similar to those familiar in cold-worked copper, were seen occasionally in the alpha phase of the "degenerate subscale." Apparently the differential shrinkage of the metal and oxide, when the former is a continuous phase, results in plastic deformation below the recrystallization temperature.

14. *Refinement of Alpha Grains*.—A refinement of the grain size of the alpha phase, next to the zone of oxidation in low-zinc samples oxidized in the air at 700°C., was found in several samples. This behavior has been observed previously⁵ and has not been explained satisfactorily.

15. *Cracking of Brittle Metallic Phases*.—Alloys predominating in the brittle gamma and epsilon phases usually were cracked throughout (Figs. 6, 7, 8 and 9). The effects of oxidation sometimes penetrated deeply along the surfaces of the cracks. This condition has been ignored in making the drawings of Figs. 1a and 1b.

16. *Oxidation of the Eta Phase in Epsilon + Eta Alloys*.—The only instance of the independent oxidation of the minor phase of a duplex alloy seen in these studies was that of the oxidation of the eta phase in alloy 90, Fig. 6.

17. *Influence of the Time of Oxidation*.—Brief studies of the influence of time at temperature, Table 1, upon the thickness of the scales have revealed marked irreg-

ularity. Most of the observations were made with the copper-rich alloys. In some cases the scales appeared to grow more or less regularly; elsewhere little or no increase in thickness was seen after two and four times the initial heating period; occasionally the scales found in the longest treatments were actually thinner than those produced in shorter intervals. The restraining influence of continuous layers of zinc oxide coupled with spalling due to temperature oscillations and the lateral growth of scales is probably responsible for these irregularities.

18. *A Paradox*.—It is interesting that the depth to which the metal is affected by oxidation is greater when access to oxygen is restricted than when air flows freely over the metal. A possible explanation of this paradox has been suggested above, in the protective action of zinc oxide when it forms on the surface together with the tendency for zinc to vaporize away from the surface without forming an oxide film when the oxygen pressure is low. Some of the air-oxidized samples developed, on the surfaces upon which they rested in the furnace, scales similar to those resulting from "pack" oxidation. This is significant because it shows that the two extremes represented in these studies may be encountered in ordinary annealing practice or where copper-zinc alloys are used at high temperatures under oxidizing conditions.

19. *Liquation*.—Few cases of oxidation in the presence of liquation were examined (Figs. 8b and 9b). Oxidation of the liquid phase appears to be greatly accelerated over the oxidation of the solid phases. In pack oxidation the zinc oxide seems to form as solid particles dispersed throughout the liquid.

20. *Phase Changes during Cooling*.—Many of the alloys obviously underwent phase changes during cooling. These have been ignored in the interpretation of the structures; i.e., the structures have been viewed as they must have been at the

TABLE I.—*Analyses and Oxidation Treatments*

Alloy Number (Nominal Zinc Content)	Weight Per Cent Copper	Weight Per Cent Zinc (by Difference)	Duration of Oxidation in Hours at Temperature Indicated. Both Conditions of Oxidation Apply Except Where Marked: (a) in Air Only, (b) in Cu ₂ O Powder Only						
			300°C.	400°C.	500°C.	600°C.	700°C.	800°C.	900°C.
10	89.28	10.72	2,160	336 624 672 1,344	135 336 360(b)	96 168 192 384	48 96 216	24 48 96 290	6 12 24
14	86.65	13.35	2,160	336(a)	135 336 360(b)	none	48 192(a)	24 48 96	6 12 24
18	81.66	18.34	2,160	336(a)	135 336 360(b)	none	48 192(a)	24 48 96	6 12 24
24	76.47	24.53	2,160	336 624 672 1,344	135 336 241	96 168 192 384	48 96 216	24 48 96 290	6 12 24
30	69.29	30.71	2,160	336 624 672 1,344	135 241 336 360(b)	96 168 192 384	48 92 192(a) 216	24 48 96 290	6 12 24
40	59.24	40.76	2,160	624	241 336 360(b)	168	96	48(a)	6 12 24
45	53.53	46.47	2,160	624	336 360(b)	168	96	48	none
48	51.15	48.85	2,160	624	241 336	168	96	48(a)	none
50	49.68	50.32	2,160	624	336	168	96	48	none
55	44.29	55.71	2,160	624	336	168	96	48	none
60	40.75	59.25	2,160	624	336	168	96	48	none
65	36.24	63.76	2,160	624	336	168	96	48	none
70	30.90	69.10	2,160	624	336	168	96	none	none
75	25.50	74.50	2,160	624	241 336	168	96	none	none
80	19.72	80.28	2,160	624	241 336	none	none	none	none
90	10.15	89.85	2,160	624	336	none	none	none	none
95	4.35	95.65	2,160	624	336	none	none	none	none
98	2.38	97.62	2,160	624	336	none	none	none	none

oxidizing temperature. Recrystallization of the metal phase, of course, has accompanied oxidation in the cold-rolled alloys. No attempts have been made to determine what effect this may have had upon the resultant scale structures.

DISCUSSION OF THE OBSERVATIONS

It is now possible to propose an elementary outline of the general process of oxidation in copper-zinc alloys, based upon

the present observations together with previous knowledge of the mechanism of oxidation in simple systems.

a. Copper oxide appears only in the external scale and then only when the oxygen pressure in the attacking atmosphere is above the decomposition pressure of cuprous oxide and at the same time the zinc delivery to the surface is inadequate to permit the formation of a continuous film of zinc oxide.

b. Zinc is delivered to the front of reaction by diffusion through the metal. This means that its rate of delivery increases with rising temperature and with an increased concentration gradient; the concentration gradient is, of course, steepest at the beginning of oxidation and in those alloys richest in zinc.

c. Oxygen is delivered to the front of reaction in one or more of several ways, depending upon the circumstances: (1) by direct contact of the gas at or in front of an open surface either external or within a crevice, (2) by the decomposition of cuprous oxide in contact with zinc, or (3) by diffusion through the metal.*

d. Where zinc and oxygen meet in sufficient concentration, zinc oxide forms. This may be: (1) within the metal whereupon a true subscale forms, (2) at a surface where a true external scale forms, or (3) beyond a surface (an external surface, a crevice, or within a cavity) where the zinc vapor oxidizes.

e. A continuous film of zinc oxide provides a barrier to the diffusion of the reactants; its growth is therefore slow.

f. The withdrawal of zinc from alloys containing in excess of 10 per cent of zinc results in the formation of cavities which are larger, more elongated perpendicular to the surface, and more interconnecting, the greater the zinc content of the alloy.

g. The deposition of zinc oxide within a metal matrix or within holes in the metal causes the latter to expand and thus provides the stresses necessary to bring about spalling.

h. Where zinc oxide deposits as a mixture with metal, it tends to become the continuous constituent periodically (Liesegang

structure), and spalling cracks follow such zones.

i. The precipitation of zinc oxide within the alpha phase of the alloy occurs generally at high temperatures and chiefly at grain boundaries at low temperatures.

j. When zinc is being withdrawn from the alloy at a relatively high rate, a complete series of the possible metallic phases, as dictated by the phase diagram, is formed in concentric shells, from alpha (at the outside) to the phase present in the core alloy at the center. If the outward diffusion of zinc is retarded by a protective film of zinc oxide, the composition of the core alloy is maintained to the interface with the oxide.

With certain evident exceptions, these factors are active over the entire range of alloy compositions, but the relative importance of each differs with the composition of the alloy, the temperature of oxidation and the oxygen concentration of the atmosphere. Moreover, the details of the process must change with time, during oxidation, for whenever a barrier of zinc oxide is established, the reaction is greatly retarded and then accelerates again when, through spalling or spheroidization, the barrier is broken. In "pack" oxidation the outer layers of the scale grow out of the debris of the inner layers and these in turn must change in the character of the voids developed in them and the degree of subsequent expansion as the zinc concentration gradient becomes less steep. Superimposed upon these complications is the influence of the shape of the specimen upon its response to the contracting and expanding forces that lead to spalling.

Clearly, there is ample reason to expect the rates of oxidation of the copper-zinc alloys to be erratic and difficult to reproduce.

SUMMARY

The structures of copper-zinc alloys containing from 10 to 98 per cent of zinc,

*In connection with the last of these processes, it should be pointed out that the solubility of oxygen is considerable only in substantially pure copper and that the diffusion of oxygen through the metallic phases containing zinc must, therefore, be small compared with that through the copper that has been freed from zinc in the course of oxidation.

after oxidation in the air and also in a closed vessel containing cuprous oxide, at temperatures from 300° to 900°C., have been described. Based upon these observations, an elementary outline of the mechanism of oxidation has been proposed.

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Grain Growth and Recrystallization of 70-30 Cartridge Brass

By R. S. FRENCH*

(New York Meeting, February 1944)

THE purpose of this paper is to present data that have been obtained during the past two years concerning the effects of prior cold-work and temperature and time of anneal upon the recrystallization and grain growth of 70-30 cartridge brass. It was desirable to study certain of these phases so that an accurate picture of the principles of the subject could be shown. The work is not intended to provide explicit annealing data, but to provide material examples that may help to clarify analogous problems concerning this alloy. Specifications often set limitations upon the grain size of annealed materials because of the importance of grain size upon subsequent manufacturing operations. It was, therefore, worth while to study the variables that affect the recrystallized grain size of this material.

C. H. Mathewson and A. Phillips,¹ W. R. Webster,² and others have presented annealing characteristic curves of this alloy. A recent typical curve presented by R. S. Pratt³ is shown in Fig. 1. The tensile properties and grain sizes are shown as functions of the annealing temperature. Such curves serve as a useful guide in determining the physical properties of annealed material, but as they are made generally under carefully controlled laboratory conditions they do not indicate the

performance of metal annealed in a mill muffle, where such conditions as amounts of metal, heating time and temperature may differ.

Study of the effect of time and temperature upon grain growth and subsequent recrystallization was made with a coil of metal having the following analysis: 70.04 per cent copper; 0.007 lead; 0.007 iron; 0.00 tin; 0.00 silicon; 0.001 nickel; 0.000 phosphorus; balance zinc. The sample coil was obtained from metal that had been rerolled from hot-rolled mill stock, and was received at 0.228-in. gauge, soft, with a grain size of 0.125 mm. This material was then rolled 43.5 per cent to 0.129-in. gauge and annealed to a 0.053-mm. grain size. In this condition, samples were cut and used in all of the experimental work reported in this paper.

TIME

The first study was of crystal growth at a constant temperature over a moderate length of time. Material was cut from the stock coil at 0.129-in. size and rolled 75 per cent hard to 0.032-in. gauge. From this piece small samples were cut $\frac{1}{2}$ by 2 in., suitable for grain-size determinations. Twelve samples were placed in an electric furnace uniformly across the width, approximately an inch from the floor. A thermocouple was wired to the center sample, so that the approximate metal temperature could be followed. At various

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* Bridgeport Brass Co., Bridgeport, Conn.

¹ References are at the end of the paper.

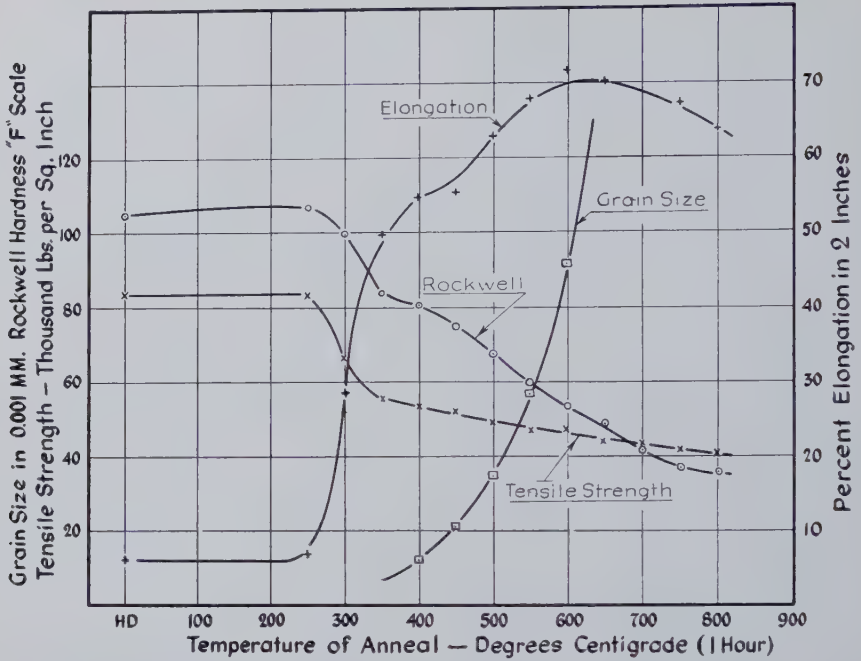


FIG. 1.—CHARACTERISTIC ANNEALING CURVES FOR 70-30 CARTRIDGE BRASS. Showing effect of annealing upon tensile properties and grain size of cold-rolled material. The metal had previously been cold-rolled 50 per cent reduction in gauge, 0.080-mm. grain size.

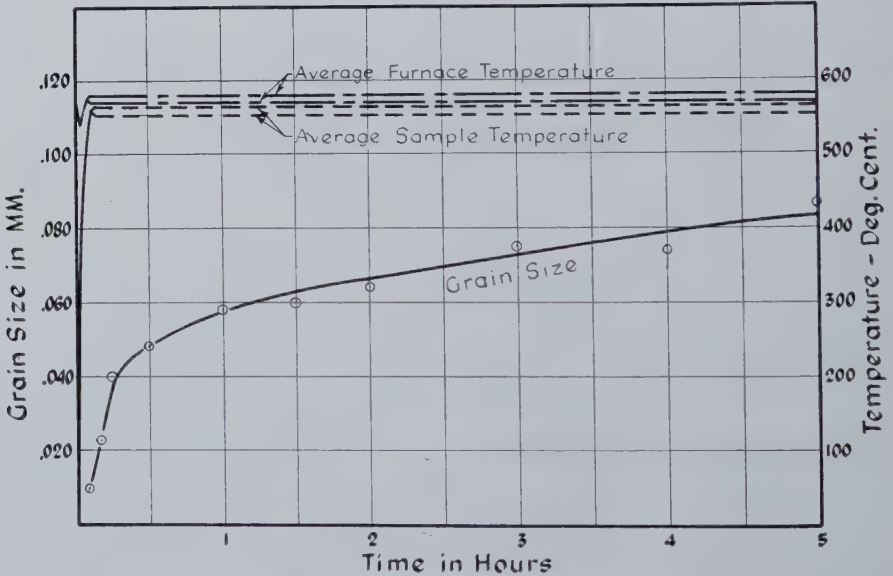


FIG. 2.—CURVE SHOWING EFFECT OF TIME UPON GRAIN SIZE OF CARTRIDGE BRASS SAMPLE HELD AT A CONSTANT TEMPERATURE.

Prior to the anneal, the material had received a 75 per cent reduction in gauge by cold-rolling, 0.053-mm. grain size.

times up to 5 hr., samples were removed from the furnace by attached wires and allowed to air cool. Fig. 2 shows the results

uniformly, although as time increased there was an indication of a decreasing rate of growth. The results of this series

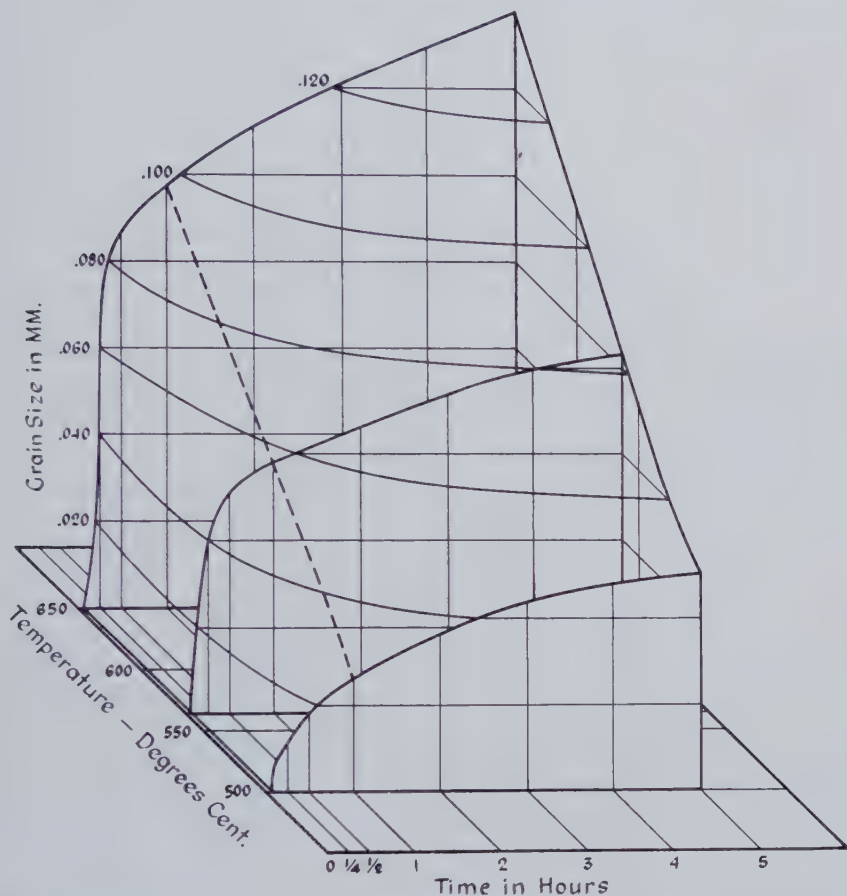


FIG. 3.—GRAIN GROWTH OF CARTRIDGE BRASS AS AFFECTED BY TIME AND TEMPERATURE OF ANNEAL.

The material was annealed to an 0.053-mm. grain size, cold-rolled 75 per cent hard to 0.050-in. gauge and annealed as indicated.

obtained using a furnace temperature of 575°C. The resultant grain size, and average metal and furnace temperatures are shown plotted against time. The thermocouple and its attached sample required about 1/4 hr. to reach a constant temperature. Recrystallization was complete within the first 2 min., and this was followed by a 30-min. period of active growth to 0.040 mm. The grain size during the 1 to 5-hr. period increased slowly, and more or less

TABLE I.—Results of Annealing Tests at Constant Temperature

Furnace Temperature, Deg. C.	Approximate Time to Heat Sample, Min.	Average Sample Temperature, Deg. C.	Grain Size after Initial Growth, Mm.	Time of Initial Growth, Approx., Min.	Grain Size after 3-hour Period, Mm.	Grain Size after 5-hour Period, Mm.
500	7	500	0.018	30	0.045	0.050
575	7	560	0.040	15	0.075	0.087
655	15	635	0.087	30	0.120	0.140

and two other temperature series are shown in Table 1.

Figure 3 is a replot of the data in which the grain size values have been plotted to

can be seen that extremely coarse grains can be obtained when operating in regions of very high temperatures and long-time anneals. It is beyond the scope of this

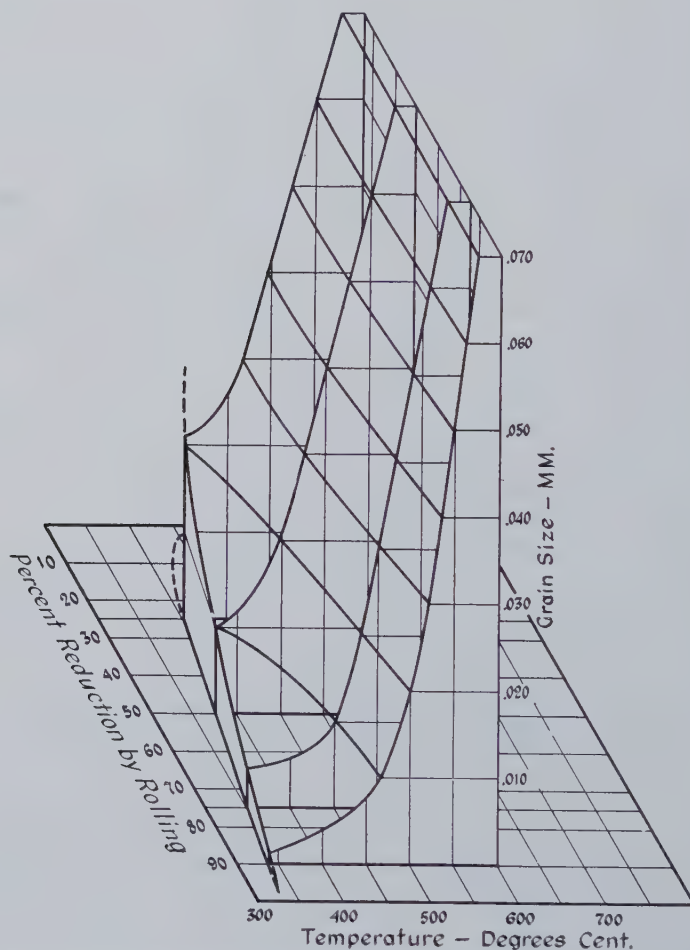


FIG. 4.—GRAIN GROWTH OF CARTRIDGE BRASS AS AFFECTED BY PRIOR REDUCTION BY COLD-ROLLING AND TEMPERATURE OF ANNEAL.

The material had an 0.053-mm. grain size at 0.129-in. gauge and was rolled and annealed for one-hour periods as indicated.

form a three-dimensional diagram against temperature and time of anneal. The dotted line on the diagram represents the customary curve of temperature vs. grain size for 1-hr. anneals shown in Fig. 1, over a very narrow region of temperatures. By comparing the 1-hr. and 5-hr. curves, it

paper to discuss specifically the effect of impurities upon crystal growth,^{4,5} but it should be pointed out that in a consideration of other brasses in which the purity is not as high as in cartridge brass the presence of many elements, intentionally or unintentionally present, may also have

quite an effect upon the rate of grain growth, and so becomes another important variable in a consideration of a sample's annealed properties.

cold-rolling from the soft, 0.129-in. size. Samples of this material were annealed at various temperatures for one hour, and from them grain size samples were pre-

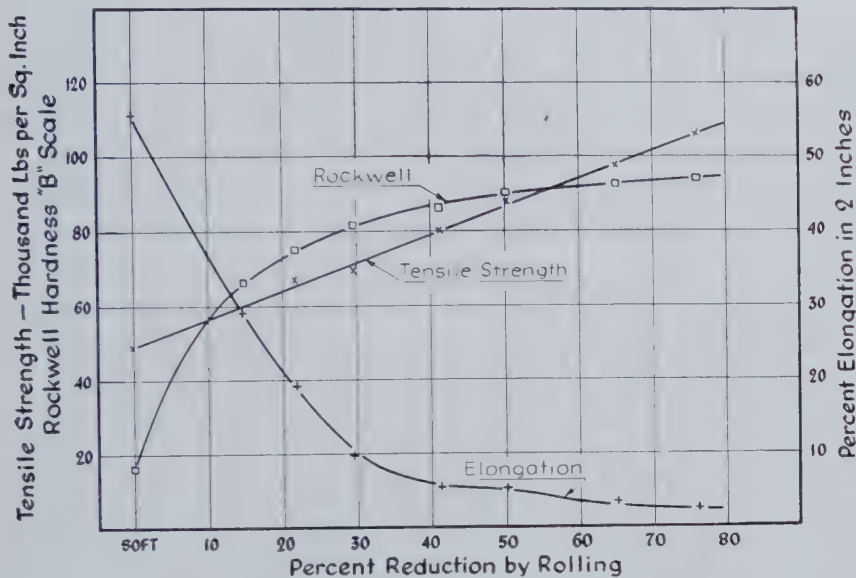


FIG. 5.—CHARACTERISTIC ROLLING CURVES OF CARTRIDGE BRASS.

Material received soft at 0.228-in. gauge and 0.125-mm. grain size, rolled to 0.129-in. gauge, annealed to 0.053-mm. grain size, and rolled as indicated.

COLD-WORK

A second study was made to show the effect of prior cold-work upon the annealed grain size. Bassett and Davis⁶ were among the first investigators to report that the condition of the metal prior to a low-temperature anneal had an effect upon the final hardness and grain size of brass, and very recently Maurice Cook and T. L. Richards⁷ have presented a comprehensive paper upon the effect of a wide range of prior reductions by cold-rolling upon the directionality characteristics of the subsequently annealed 70-30 brass samples.

The present tests were made at a constant annealing time of 1 hr. using samples with four different degrees of cold-work. Samples were cut from the stock coil and given 25 per cent, 50 per cent, 75 per cent, and 90 per cent respective reductions in gauge by

pared. The results plotted in a three-dimensional diagram are shown in Fig. 4, grain size being plotted against temperature for each of the reductions. While the prior reduction by cold-work does not seem to affect grain size greatly at the higher temperatures, it does affect the grain size and temperature of recrystallization. Fig. 4 illustrates that as the amount of prior cold-working increases, the size of the recrystallized grain and the necessary temperature of recrystallization decreases when time is held constant.

Bassett and Davis,⁶ F. G. Smith,⁸ C. Upthegrove and G. Harbert,⁹ and others have shown also that the grain size prior to cold-working and subsequent annealing affects the resultant recrystallization and grain growth of cartridge brass. Time has prevented work on materials of other than

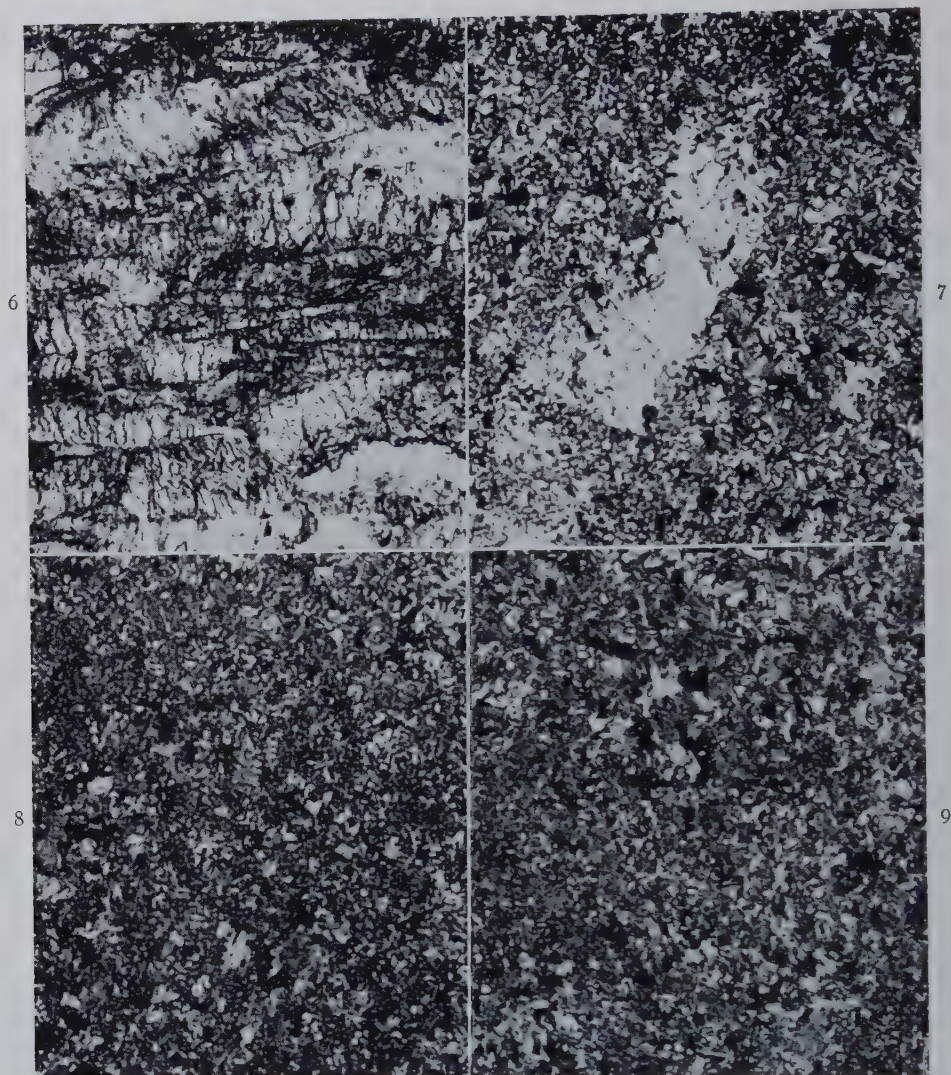


FIG. 6.—70-30 CARTRIDGE BRASS AS COLD-ROLLED 76 PER CENT HARD. $\times 250$.

FIG. 7.—70-30 CARTRIDGE BRASS COLD-ROLLED 76 PER CENT HARD.

Annealed for 30 min. at 325°C . Rockwell F-92; 97 per cent recrystallized. $\times 250$.*

FIG. 8.—70-30 CARTRIDGE BRASS ROLLED 76 PER CENT HARD AND ANNEALED AT 325°C . FOR 40 MINUTES ROCKWELL F-91.5; 0.005-MM. GRAIN SIZE. $\times 250$.

FIG. 9.—70-30 CARTRIDGE BRASS ROLLED 76 PER CENT HARD AND ANNEALED 325°C . FOR 50 MINUTES. ROCKWELL F-91.0; 0.007-MM. AVERAGE GRAIN SIZE. $\times 250$.

All samples etched with $\text{NH}_4\text{OH} \cdot \text{H}_2\text{O}_2$.

* Percentages given are only approximate and are estimates of a much larger surface area than are included on these photomicrographs.

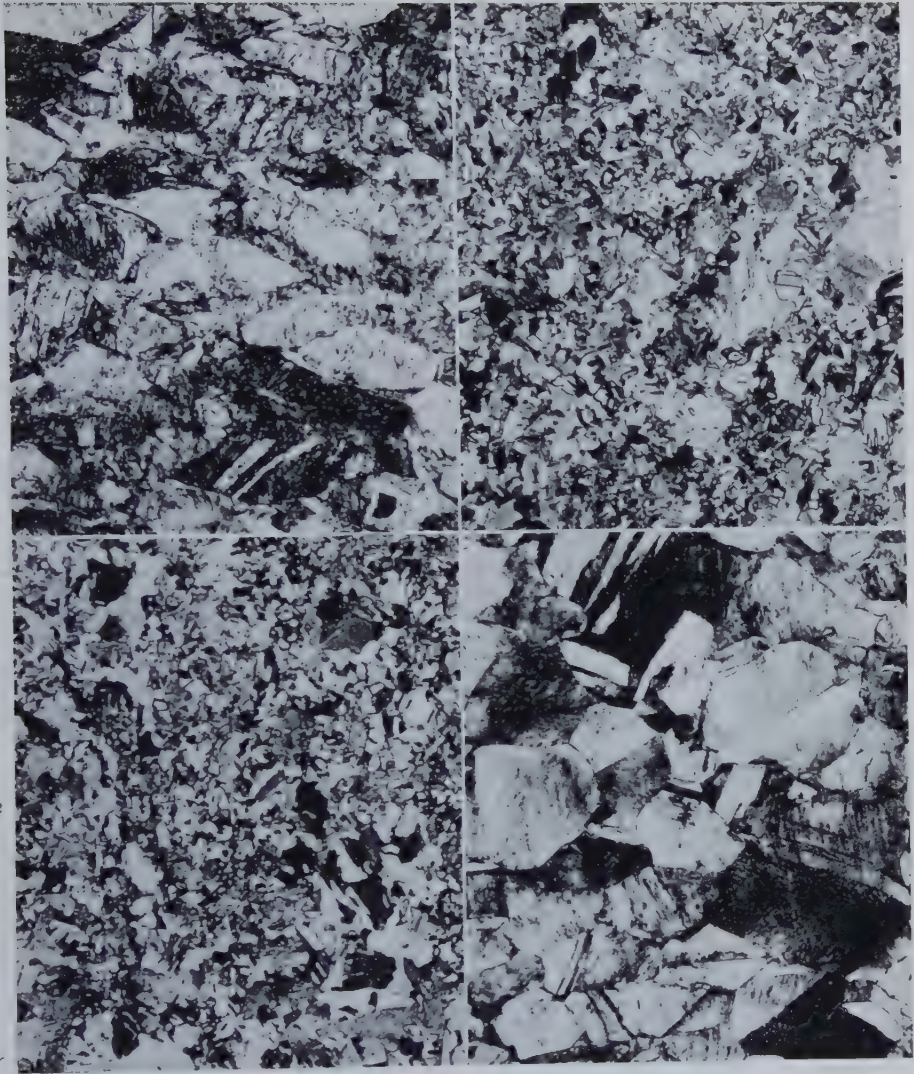


FIG. 10.—70-30 CARTRIDGE BRASS ROLLED 50.4 PER CENT HARD. $\times 200$.

FIG. 11.—70-30 CARTRIDGE BRASS ROLLED 50.4 PER CENT HARD AND ANNEALED AT 325°C . FOR 160 MINUTES. ROCKWELL F-86; 98 PER CENT RECRYSTALLIZED. $\times 200$.

FIG. 12.—70-30 CARTRIDGE BRASS ROLLED 50.4 PER CENT HARD AND ANNEALED AT 325°C . FOR 180 MINUTES. $\times 200$.

Rockwell F-85; 0.010-mm. grain size approximately.

FIG. 13.—70-30 CARTRIDGE BRASS, ROLLED 29.5 PER CENT HARD. $\times 200$.

0.053-mm. grain size but it is also a variable that must be taken into consideration.

RECRYSTALLIZATION

There are well-known laws concerning recrystallization, and various authors have shown the correlation of some of these factors in brass and ferrous alloys.¹⁰⁻¹³ The question arose as to the exact time of complete recrystallization for cartridge brass as affected by changes of temperature and amounts of prior deformation.

A set of increasingly worked material was rolled from the stock coil, and provided a group that could be cut up and annealed for various lengths of time at various temperatures. The physical properties of these samples had been plotted³ as a rolling characteristic curve, shown in Fig. 5. At the start of the work, it was necessary to find a satisfactory heating medium at an operating temperature low enough to allow recrystallization to take place slowly and permit the study to be made. A salt bath with a temperature range from 200° to 500°C. proved quite satisfactory and was used throughout the tests. To establish the curves, samples rolled 50.4 per cent, 65.2 per cent, and 76 per cent hard were annealed at 300°, 350°, and 400°C., for 2½, 5, 8, 10, and 20 min., respectively. This preliminary work more or less established the region of some of the recrystallization curves. Samples were all subjected to Rockwell hardness tests and polished for microexamination. Very few of these samples were completely recrystallized, but by following the Rockwell hardness values and estimating the percentage of residual cold-worked grains in each of the

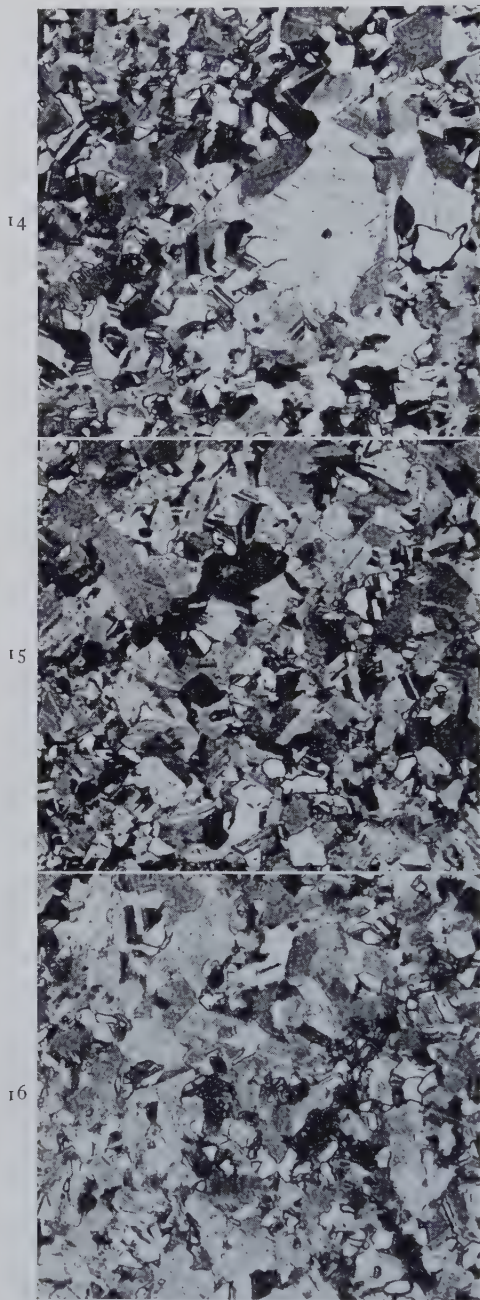


FIG. 14.—70-30 CARTRIDGE BRASS, ROLLED 29.5 PER CENT HARD, AND ANNEALED AT 400°C. FOR 15 MINUTES. $\times 200$.

Rockwell F-81; 98 per cent recrystallized.

FIG. 15.—70-30 CARTRIDGE BRASS, ROLLED 29.5 PER CENT HARD AND ANNEALED AT 400°C. FOR 17 MINUTES.

Rockwell F-81; 0.018-mm. grain size average. $\times 200$.

FIG. 16.—70-30 CARTRIDGE BRASS, 29.5 PER CENT HARD, ANNEALED AT 400°C. FOR 20 MINUTES.

Rockwell F-80; 0.020-mm. grain size, average. $\times 200$.

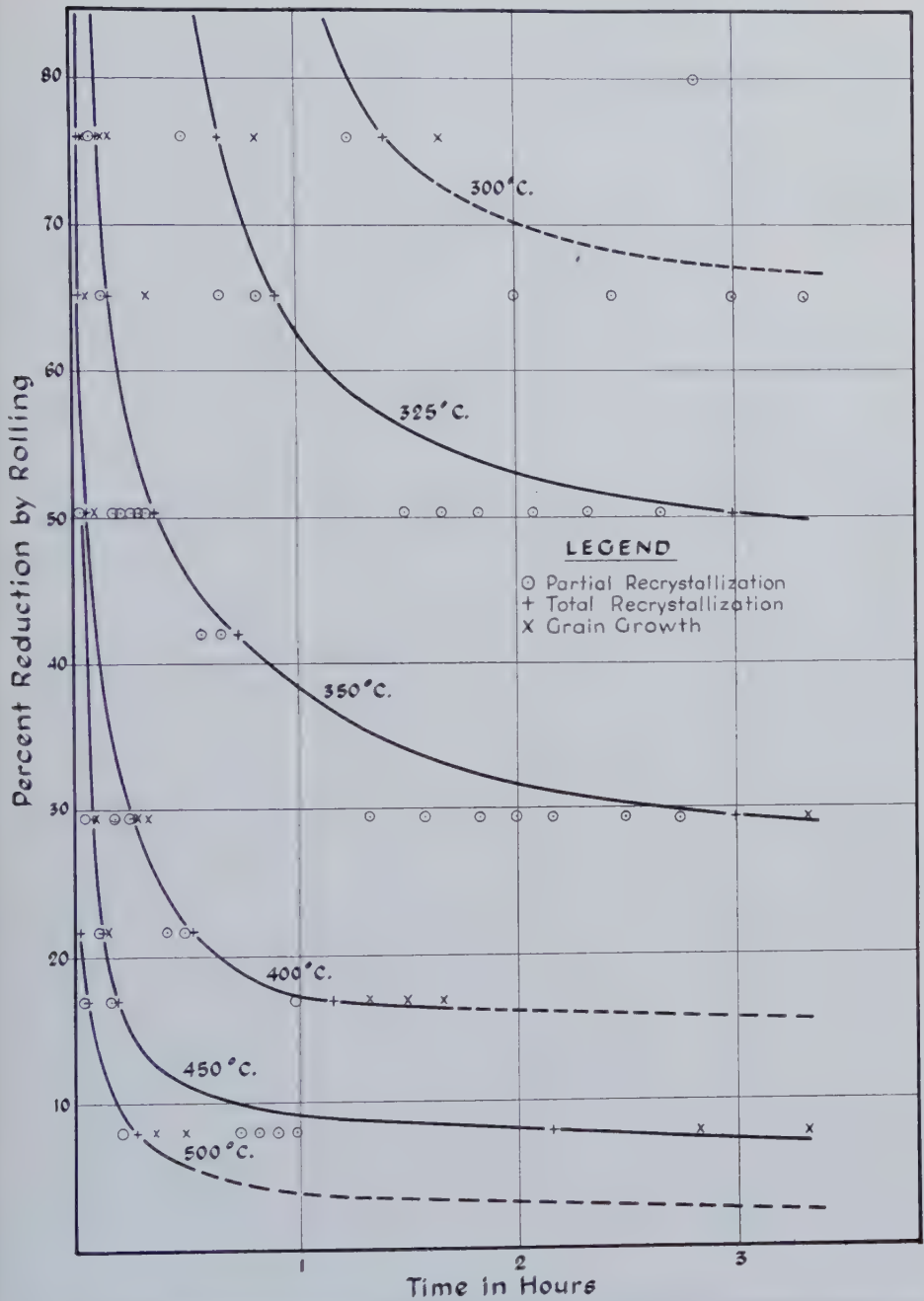


FIG. 17.—GROUP OF CURVES SHOWING EFFECT OF AT-READY REDUCTION AND TEMPERATURE UPON TIME FOR COMPLETE RECRYSTALLIZATION OF CARTRIDGE BRASS

Material annealed to 0.053-mm. grain size at 0.129-inch gauge and rolled and annealed as indicated.

partly recrystallized samples, estimations could be made as to the time necessary for complete recrystallization for any of the temperatures or reductions. Then in a

later, material cold-rolled 25 per cent or more recrystallized with a grain size of 0.030 mm. or finer, so that it was comparatively easy to detect grains that had not

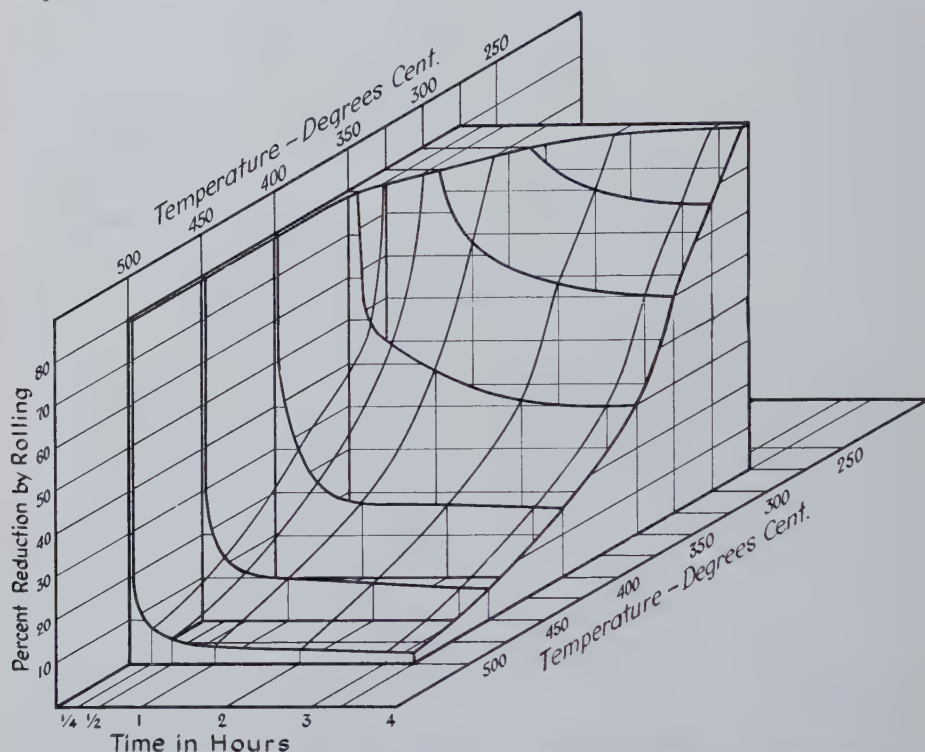


FIG. 18.—TIME OF COMPLETE RECRYSTALLIZATION OF CARTRIDGE BRASS VS. TEMPERATURE AND PERCENTAGE PRIOR REDUCTION BY COLD-ROLLING.

A diagram of the data shown in Fig. 17.

similar manner, these times were checked. Subsequently material 8, 17, 21.7, 29.5, and 42 per cent hard was also studied. The data obtained are reported in Table 2. The time to heat and recrystallize a sample at temperatures and reductions that allow for immediate recrystallization was about 2 min., so that all the curves approach that limit. (Strain lines in some grains persisted until a very short time before grain growth began, and any particular sample that showed any traces of cold-work was disregarded.)

A problem developed in the determination of the time of recrystallization in the light reduction samples. As will be shown

recrystallized, but it was very difficult with the material 8 to 17 per cent hard, in which the annealed grain was only slightly smaller, if at all, than the size of the hard grain. It was found by observation that in these two low reductions uniform grain growth took place after the completion of recrystallization; therefore samples were annealed for various times, and then polished, etched, and counted; the time for total recrystallization being taken at the time grain growth was first observed. Mathewson and Phillips¹ suggested that material lightly cold-worked lacked sufficient "inner surfaces" of slip to bring about recrystallization as such, and healed

upon annealing without reorientation of the grains. Likewise, Eastwood, Bousu and Eddy¹² and recently S. E. Maddigan and A. I. Blank¹⁴ also have shown that the formation of nuclei are unnecessary in the softening of such material. In the present work the times necessary to anneal the lightly worked material and to start grain growth seem to fit smoothly in with the other recrystallization data.

Pictures have been taken showing how three points in Fig. 17 were determined. Figs. 7, 8, and 9 show the results obtained when material 76.0 per cent hard (Fig. 6) is annealed at 325°C. for 30, 40, and 50-min. periods, respectively. Recrystallization occurred in Fig. 8 after a 40-min. anneal at this temperature. Fig. 7 shows about 97 per cent recrystallization while Fig. 9 shows that slight grain growth has occurred. Figs. 10, 11 and 12 show the recrystallization of a 50.4 per cent hard sample also at 325°C. These samples were annealed 160 and 180 min., respectively, and it was the sample in Fig. 12 that showed 100 per cent recrystallization. Material 29.5 per cent hard (Fig. 13), recrystallizing at the 400°C. temperature, required an annealing period of 17 min. Fig. 14, a sample annealed 15 min., shows again an area of cold-work. Fig. 15 is recrystallized and Fig. 16, after a 20-min. anneal, shows some grain growth. There may be a question concerning the lack of uniformity of these completely recrystallized structures. Growing grains do tend to become more equiaxed and uniform, and, realizing that recrystallization begins at points of high stress concentration, it seems evident from the photomicrographs of the hard material that it would be impossible to expect uniformity in the newly born crystals; i.e., some have a head start in growth.

Figs. 17 and 18 show the results of these tests as plotted. Fig. 18 is a three-dimensional view of Fig. 17 and serves as a model only, but gives a very clear picture

of the behavior of recrystallization as affected by the three variables, time, temperature and percentage of reduction. In Fig. 17, the amount of cold-work, indicated as percentage reduction of gauge is plotted against time in hours and minutes, and the time necessary for recrystallization is plotted according to the temperatures of the test.

RECRYSTALLIZED GRAIN SIZE

The grain sizes of all the completely recrystallized samples shown in Fig. 17

TABLE 2.—Points Obtained for Total Recrystallization Series

Temperature, Deg. C.	Reduction, Per Cent	Time	Grain Size, Mm.	Hardness, Rockwell F	Sample No.	Gauge, In.
		Hr. Min.				
300	76.0	1 25	0.005	94.0	3063	0.031
325	76.0	40	0.005	91.5	326X1	0.031
325	65.2	55	0.007	90.5	325X1	0.045
325	50.4	3 00	0.010	85.0	324X10	0.064
350	76.0	7	0.006	94.0	3563	0.031
350	65.2	10	0.010	91.0	3551	0.045
350	50.4	22	0.013	87.0	3544	0.064
350	42.0	45	0.013	88.5	357X2	0.075
350	29.5	3 00	0.020	80.0	353X8	0.091
400	76.0	2	0.004	92.0	4068	0.031
400	65.2	2	0.008	90.0	40581	0.045
400	50.4	4	0.010	86.5	4049	0.064
400	29.5	16	0.017	81.0	4032	0.091
400	21.7	32	0.026	77.5	4023	0.101
400	17.0	1 10	0.037	77.0	401X1	0.107
450	29.5	5	0.021	79.0	4534	0.091
450	21.7	8	0.024	76.5	452X1	0.101
450	17.0	12	0.032	75.0	451X1	0.107
450	8.0	2 10	0.054	63.0	458X4	0.119
500	17.0	4	0.033	72.5	501X1	0.107
500	8.0	17	0.052	67.0	508X1	0.119

were counted by four laboratory assistants and the results were averaged (Table 2). A curve of these values plotted against the amount of prior cold-work is similar to one previously reported by Eastwood, Bousu and Eddy.¹² This curve (Fig. 19) shows that the size of the crystals increases as the amount of prior deformation is decreased (Fig. 4) and recrystallized grain size is independent of the temperature of anneal. The indications seem to be that

in fully annealed lightly worked material the grain size might be very large.

INITIAL SOFTENING BY ANNEAL

Fig. 18, the three-dimensional diagram for total recrystallization, shows that

lization would be defined as an average one-point drop in F Rockwell from the hard state, as rolled. Any slight rise in hardness due to relief of stress of recovery before softening was disregarded and the annealing was carried until a

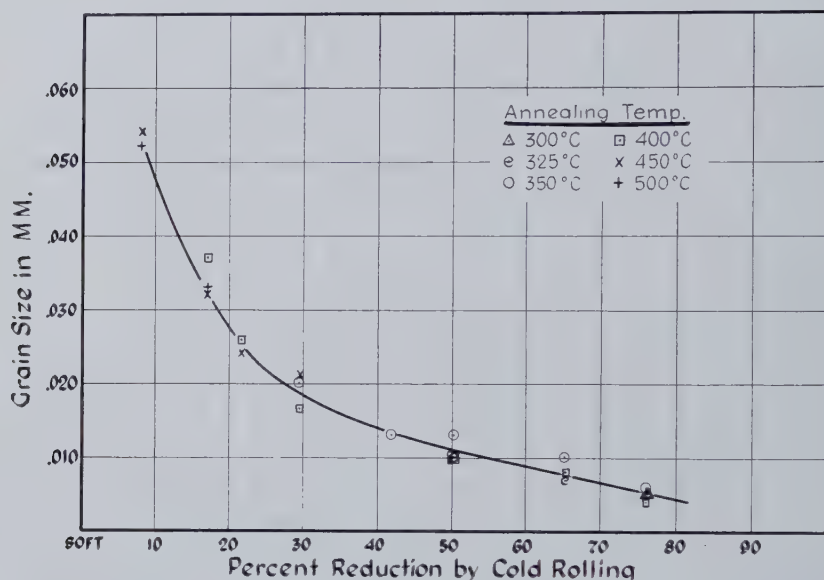


FIG. 19.—EFFECT OF PRIOR REDUCTION AND OF TEMPERATURE UPON INITIAL GRAIN SIZE OF RECRYSTALLIZED CARTRIDGE BRASS.

Material had been annealed to an 0.053-mm. grain size and rolled as indicated prior to complete recrystallization anneal.

above the diagram there lies a region of grain growth and below a region of partially recrystallized metal. After the completion of this diagram, work was continued and data gathered for a diagram to show how percentage reduction by cold-work and temperature of anneal affect the time of the early stages of recrystallization. Mathewson and Phillips¹ had investigated the time necessary to start softening of a 40 per cent hard 70-30 brass annealed at various temperatures from 225° to 325°C., by annealing at the given temperature until a three-point drop in scleroscopic hardness was obtained.

X-ray equipment not being available in our laboratory, it was arbitrarily decided that the beginning of recrystal-

one-point drop from the original hard value was obtained. It was felt that this basis was more practicable than that of allowing the metal to recrystallize far enough actually to see new grains, for this would have exceeded useful relief-annealing temperatures and much softening would have occurred. The question may be raised that a one-point change exceeds the accuracy of a Rockwell machine. The rolled brass was found to be perfectly homogeneous, the Rockwell machine was checked daily, and all samples were tested at least three times before and after the anneal was made. The anneals were made exactly as previously described on similar material cold-rolled from the coil.

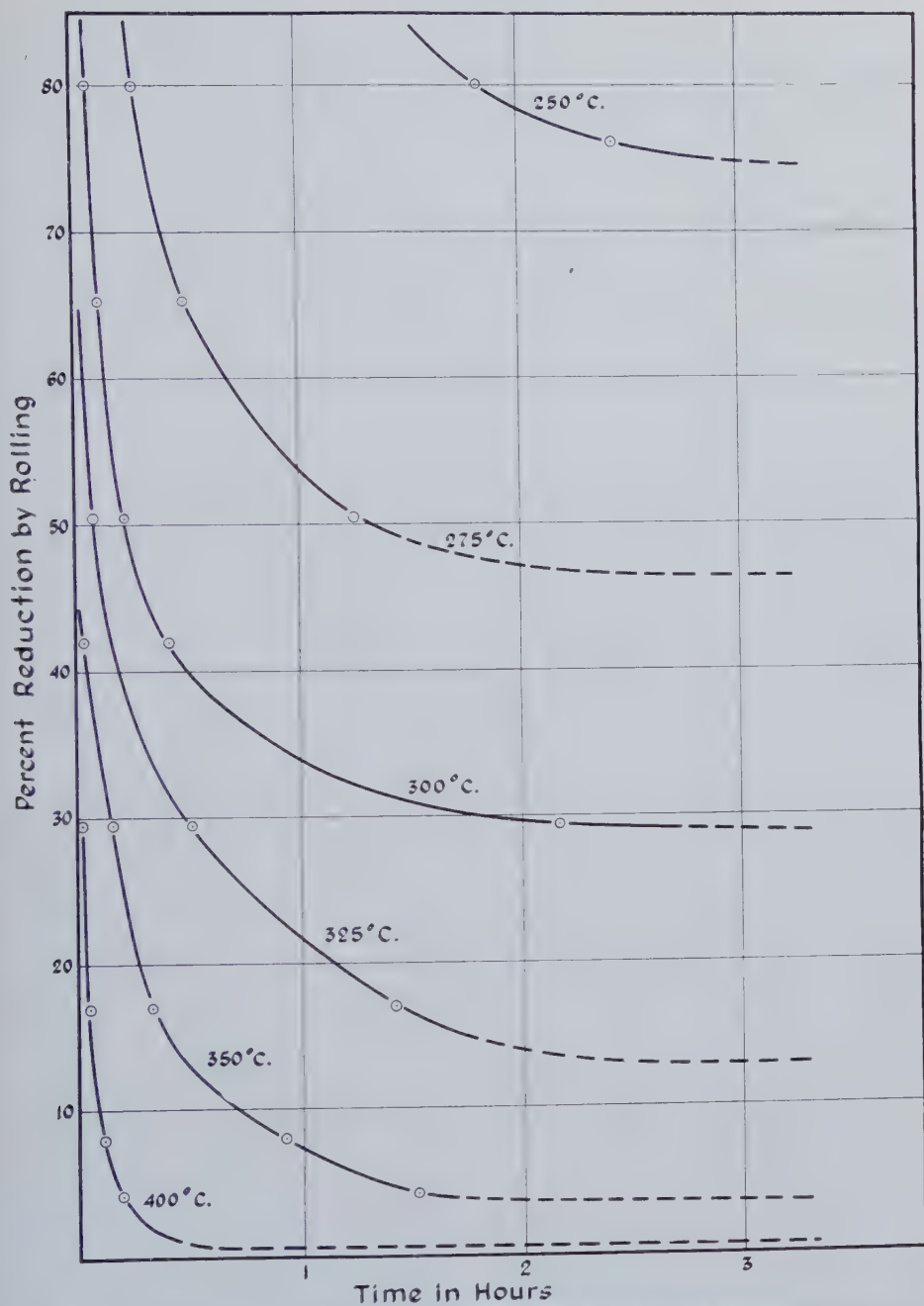


FIG. 20.—EFFECT OF PRIOR REDUCTION AND TEMPERATURE UPON TIME OF INITIAL SOFTENING OF RECRYSTALLIZATION OF CARTRIDGE BRASS.

Material had been annealed to an 0.053-mm. grain size at 0.129-inch gauge and was rolled and annealed as indicated.

Table 3 shows the tabulated results obtained and Figs. 20 and 21 the results plotted in the two and three dimensions, as before. These curves indicate that the

duplicated on a finer and a coarser grain-size material than was used herein (0.053 mm.). An attempt was made to treat the total recrystallization data analytically

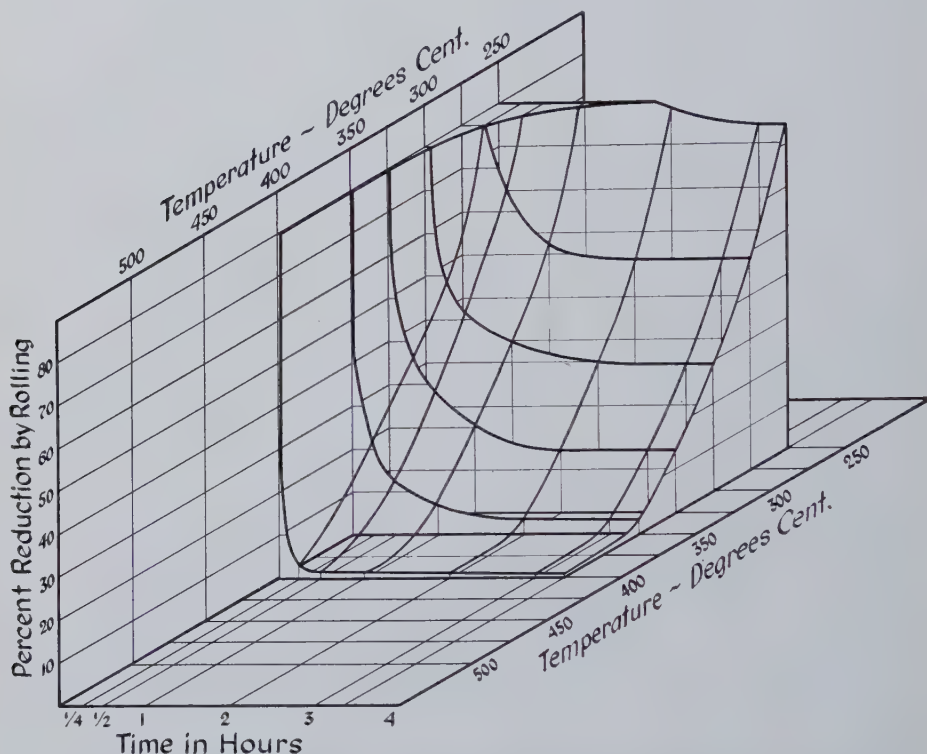


FIG. 21.—TIME OF INITIAL SOFTENING OF RECRYSTALLIZATION OF CARTRIDGE BRASS VS. TEMPERATURE AND PERCENTAGE PRIOR REDUCTION BY COLD-ROLLING.

A diagram of the data shown in Fig. 20.

well-known rules concerning complete recrystallization also concern the beginning of recrystallization. The region immediately over any temperature curve is partially recrystallized metal, while that under the curve is substantially hard material.

From these two curves on recrystallization and grain growth there have been eliminated the variables prior to cold-work, of grain size, and chemical analysis changes, etc., by the use of material from the same stock coil for all anneals; but it should be pointed out that to cover this subject completely, the work would be

but no satisfactory conclusions were reached.

SUMMARY

1. The physical properties of cartridge brass in the annealed condition are largely dependent upon the grain size.

2. Grain growth is affected by composition, the prior deformation and grain size and by the time and temperature of anneal. Grain size will be greater, the higher the temperature and the longer the time of anneal.

3. While there are other factors—such as purity, composition and grain size

TABLE 3.—Points Obtained for Initial Recrystallization Series

Temperature, Deg. C.	Reduction, Per Cent	Time		Hardness, Rockwell F		Sample No.	Gauge, In.
				Be- fore	Aft- er		
		Hr.	Min.				
250	80.0	I	50	110.5	109.5	250YI	0.0255
250	76.0	2	27	110.0	109.0	256Y2	0.031
275	80.0		16	110.5	109.5	270YI	0.0255
275	65.2		32	110.0	109.0	275YI	0.045
275	50.4	I	15	108.0	107.0	274YI	0.064
300	80.0		4	110.5	109.0	309YI	0.0255
300	65.2		6	110.0	109.0	305YI	0.045
300	50.4		13	108.0	107.0	304YI	0.064
300	42.0		25	106.0	105.0	307YI	0.075
300	29.5	2	10	102.5	101.5	303YI	0.091
325	50.4		5	108.0	107.0	324YI	0.064
325	29.5		3	103.0	102.0	323YI	0.091
325	17.0	I	25	96.0	95.0	321YI	0.107
350	42.0		2	106.0	105.0	357YI	0.075
350	29.5		9	102.0	101.0	353YI	0.091
350	17.0		19	96.0	95.0	351YI	0.107
350	8.0		55	86.5	85.5	358YI	0.119
350	4.25	I	30	81.0	80.0	3510YI	0.1235
400	29.5		I	102.0	101.0	403YI	0.091
400	17.0		3	96.0	95.0	401YI	0.107
400	8.0		6	86.0	85.0	408YI	0.119
400	4.25	II		81.0	80.0	4010YI	0.1235

prior to deformation—the time, temperature and deformation factors have been studied and shown on curves as they affect the time for the beginning and completion of recrystallization. These curves illustrate the well-known laws of recrystallization; namely, the time necessary to bring about either the beginning or completion of recrystallization is less, the greater the amount of deformation or the higher the temperature of anneal.

4. These curves for recrystallization show that under any set of conditions these three variables are dependent upon each other and are fixed.

5. The initial grain size of recrystallized material has been shown to be a function of the amount of cold-work prior to the anneal—the greater the amount of work, the finer the resultant grain.

6. Some indication has been shown that the annealing temperature of very lightly worked material is fairly high and that the resultant grain size large.

Graphs and data shown in this report should be used as examples only. The history of a sample is most important and direct use of any of these curves may cause undesired results.

The grain sizes required for cartridge-case material are generally coarser than that of the material used in this report.

It is admitted that many factors must be studied in connection with recrystallization and grain growth of the alpha crystals found in cartridge brass, but it is hoped that some light may have been thrown on the general picture of its behavior and that perhaps some inspiration for further studies of this subject may be gained from this paper.

ACKNOWLEDGMENTS

The author wishes to thank Dr. Alan Morris and Mr. Roy S. Pratt, for helpful suggestions given, and the Bridgeport Brass Co. for permission to publish these results.

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DISCUSSION

(Alan Morris presiding)

D. L. MARTIN,* Schenectady, N. Y.—The author indicates, in Figs. 1 and 4, that for a given reduction and annealing time the grain size increases with temperature, and at any

temperatures was uniform, but at intermediate temperatures a mixed grain structure was obtained.

It has been my experience that a mixed grain structure is frequently encountered in annealed silver, copper, and copper alloys. For example, in Fig. 23 is shown the mixed structure obtained in a 70-30 brass rod annealed at 800°C. for one hour. The grains in this particular sample vary in size by a ratio of about 3:1.

From a commercial standpoint the average grain size-temperature curves given in Figs. 1 and 4 may suffice, but they are of little value in studies of the effect of grain size on some property, such as creep, where a uniform grain size is necessary to properly evaluate the effect.

The discontinuous grain growth seems to be

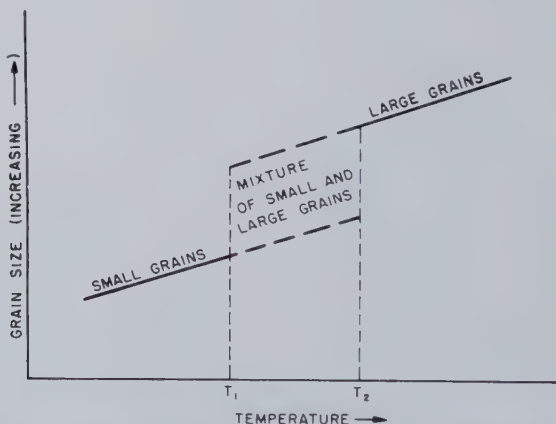


FIG. 22.—SCHEMATIC REPRESENTATION OF DISCONTINUOUS GRAIN GROWTH OF COPPER. (After Parker and Riisness.)

definite temperature of anneal the grains are uniform in size. His results on 70-30 brass agree with those by Webster, Christie and Pratt on various coppers.¹⁵ Parker and Riisness,¹⁶ on the other hand, have stated that the grain growth of commercial oxygen-free copper is discontinuous, as shown in Fig. 22. The grain size at low or high annealing tem-

related to inclusions, nonuniform plastic deformation, and preferred orientation of the grains. Whatever the factors responsible for mixed grains, it appears that they cannot always be avoided, and therefore it might be worth while to indicate on the grain-growth curves the range of grain size as well as the average grain diameter for temperatures in the mixed grains zone.

* Research Laboratory, General Electric Company.

¹⁵ W. R. Webster, J. L. Christie and R. S. Pratt: *Trans. A.I.M.E.* (1933) **104**, 166.

¹⁶ E. R. Parker and C. F. Riisness: This volume, p. 117.

R. S. FRENCH (author's reply).—The difficulties encountered by E. R. Parker and C. F. Riisness, discussed here by Mr. Martin, are familiar ones to manufacturers of non-

ferrous metal that supply material in the soft condition for cold-working operations, that degree of softness usually being specified by grain-size limits. The grain growth of certain

of these alloys can be controlled by changes in prior annealing temperatures and reductions, so that this region will not interfere with specification requirements.



FIG. 23.—DRAWN 70-30 BRASS ROD (0.750-IN DIA.) AFTER ANNEALING AT 800°C. FOR ONE HOUR.

metals and alloys, such as copper, silicon bronzes, aluminum bronzes and others is apt to be of the discontinuous type.

One of the most important factors that promote this condition is the small amount of foreign elements, purposely added or otherwise present. The author referred to two papers on this subject in the text. In many instances it is found that the region of varied grain growth

Of no such unusual interest, however, were the grain-size values recorded as shown in Figs. 1 and 4 for these particular samples of cartridge brass. The degree of uniformity at each annealing temperature was consistent with the uniformity of the standards by which they were determined, similar to those shown in plate 3, part 1 of the 1942 A.S.T.M. Standards.

Stress-corrosion Cracking of 70-30 Brass by Amines

By H. ROSENTHAL* AND A. L. JAMIESON,† JUNIOR MEMBERS A.I.M.E.

(New York Meeting, February 1944)

THE action of mercury on stressed brass to produce cracks was known before Moore, Beckinsale and Mallinson¹ showed that actual season cracking did not occur spontaneously but could be induced by ammonia. These investigators studied other substances, including diphenylamine, without finding that anything other than ammonia could cause season cracking. Grimston² reported season cracking in cartridge cases stored in wooden boxes wetted with dilute sulphuric acid pickling solution. Season cracking associated with sulphur dioxide, water vapor and air has been reported by Johnston,³ although he reported that trimethylamine and pyridine did not cause cracking. Jevons⁴ has ascribed season cracking of brass in certain instances to trimethylamine, "aldehyde amine," "ketone amine" and pyridine, but no experimental work was done evidently to prove this definitely. Pyridine was investigated by Morris,⁵ who found it to have considerable cracking power.

In the present investigation, the object was a qualitative evaluation of a number of representative amines with respect to their ability to cause season cracking. Thus it was desired only that an appreciable vapor pressure of each amine be obtained in order to make the test as severe as possible, without attempting to test equivalent concentrations for comparative purposes.

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* Associate Metallurgist, Ordnance Laboratory, Frankford Arsenal, Philadelphia, Pa.

† Metallurgist, Frankford Arsenal.

¹ References are at the end of the paper.

METHODS

Specimens

Two types of specimen were used:

1. Unannealed 70-30 brass cups formed from 0.040-in. thick sheet. Height of cup was $1\frac{3}{8}$ in. and diameter was $1\frac{1}{8}$ inches.
2. First draw pieces of caliber .50 cartridge cases in the unannealed condition (70-30 brass).

The cups were representative of a thin wall and thin base specimen, whereas the draw pieces have a thick base ($\frac{1}{4}$ in.) and a thick wall (approximately $\frac{3}{32}$ in.).

Both types of specimens contained high residual stress and cracked in less than one minute in a solution of 1 per cent mercurous nitrate and 1 per cent nitric acid provided that this was preceded by a 30-sec. pickle in 40 per cent nitric acid.

Specimens were prepared as follows: (1) degreased in trichlorethylene, (2) rinsed in H₂O, (3) pickled 5 min. in 10 per cent by volume H₂SO₄ (1.84 sp. gr.), (4) rinsed in H₂O, and (5) dried.

Amines Tested

In selecting the amines, representatives of the three series of amines and one series of substituted amines were chosen. The aliphatic series was represented by the methyl and ethyl primary, secondary and tertiary amines. These are the simplest aliphatic amines.

For the aromatic series, the phenyl primary, secondary and tertiary amines were selected as being the simplest.

The heterocyclic series was represented by pyridine, which is a simple heterocyclic base (tertiary amine).

The ethanol primary, secondary and tertiary amines were included as representatives of substituted aliphatic amines.

Test Conditions

Previous investigators^{3,6} have found that stress-corrosion of brass by ammonia is facilitated by the presence of air and water vapor. It was not known whether air and water vapor are necessary to cause corrosion cracking with amines but, since an analogous effect might well exist, it was decided to test each amine in the system: amine vapor, air, water vapor.

The specimens for each test, consisting of three cups and three draw pieces, were supported in the upper part of a Mason jar. Small tripod-shaped racks were constructed from copper wire and on these the draw pieces were supported above the bottom of the jar. The cups were suspended by a cord from the top of the jar where the end of the cord was fastened to a brass plate, which was retained on the neck of the jar just beneath the lid. This arrangement is illustrated in Fig. 1.

The draw pieces were not insulated from each other, since the three were hung on a common metallic rack. The cups, on the other hand, did not touch each other and were insulated from one another by the nonconducting cord.

Three 50-ml. Pyrex beakers were placed in the bottom of each jar to hold the reagents.

Water vapor was supplied to the atmosphere from the water placed in the beakers. The method of adding water varied according to the particular amine. The gaseous amines were obtained in a 33 per cent aqueous solution and thus required no addition of water. The water-soluble liquid amines were diluted with equal volumes of water, and the water-insoluble amines were tested by keeping two of the beakers filled with water while the other contained the amine being investigated.

It was desired that an appreciable vapor pressure of each amine be obtained to make the exposures severe. This, unfortunately, was impossible at room



FIG. 1.—ARRANGEMENT OF SPECIMENS IN MASON JAR FOR AMINE EXPOSURE TEST.

temperature because some of the amines have low vapor pressures at this temperature. To avoid this difficulty, two test temperatures were used, 100°F and 200°F.

A summary of the test conditions used for each amine is shown in Table 1.

During the test period, each jar was sealed by a glass lid clamped against a rubber gasket. Test temperatures were maintained by electrically heated, forced-circulation cabinets, which were thermostatically controlled to a variation of less than $\pm 2^\circ\text{F}$.

All the amines were obtained from the Eastman Kodak Co. except the ethanolamine, diethanolamine and triethanolamine, which were furnished by the Carbide

and Carbon Chemical Corporation. The diethanolamine was reported to contain not more than 2 per cent each of ethanolamine and triethanolamine and not less

Examination of Specimens

Specimens were examined before exposure and daily for the first 17 days of

TABLE 1.—*Test Conditions*

Amine	Test Temperature, Deg. F.	Source of Water Vapor with Amine	Quantity of Reagent Used
Methylamine (gas).....	100	33 per cent aqueous solution	75 ml.
Dimethylamine (gas).....	100	33 per cent aqueous solution	75 ml.
Trimethylamine (gas).....	100	33 per cent aqueous solution	75 ml.
Ethylamine (liquid).....	100	50 per cent aqueous solution	75 ml.
Diethylamine (liquid).....	100	50 per cent aqueous solution	75 ml.
Triethylamine (liquid).....	100	Water in beaker	50 ml. triethylamine and 25 ml. water
Aniline (Phenylamine) (liquid).....	200	Water in beaker	50 ml. aniline and 25 ml. water
Diphenylamine (solid).....	200	Water in beaker	10 grams diphenylamine and 25 ml. water
Triphenylamine (solid).....	200	Water in beaker	10 grams triphenylamine and 25 ml. water
Pyridine (liquid).....	100	50 per cent aqueous solution	75 ml.
Ethanolamine (liquid).....	200	50 per cent aqueous solution	75 ml.
Diethanolamine (liquid).....	200	50 per cent aqueous solution	75 ml.
Triethanolamine (liquid).....	200	50 per cent aqueous solution	75 ml.

TABLE 2.—*Results of Amine Exposure*

Reagent	Number of Specimens		Number of Specimens Cracked		Number of Days before Cracking		Color of Corrosion Film on Specimens
	<i>a</i>	<i>b</i>	<i>a</i>	<i>b</i>	<i>a</i>	<i>b</i>	
Methylamine.....	3	3	3	3	4	4	Light brown
Methylamine (retest).....	3	3	3	3	1	1	
Dimethylamine.....	3	3	0	1	r	45 ^d	Light brown
Trimethylamine.....	3	3	3	3	45 ^d	45 ^d	Light brown
Ethylamine.....	3	3	3	3	3	3	Spotty dark purple
Ethylamine (retest).....	3	3	3	3	2	2	
Diethylamine.....	3	3	0	0	r	r	Spotty brown
Triethylamine.....	3	3	0	0	r	r	Unchanged
Aniline (Phenylamine).....	3	3		1		12	Dark brown
			3	1	45 ^d	45 ^d	Light brown
Diphenylamine.....	3	3		1		1	
			0	0	r	17	
Diphenylamine (retest).....	3	3		0	s	s	
Triphenylamine.....	3	3	0	1	r	45 ^d	Purplish red
Pyridine.....	3	3	0	0	s	s	Dark brown
Ethanolamine.....	3	3	3	3	4	4	Dark brown
Ethanolamine (retest).....	3	3		2		3	
Diethanolamine.....	3	3		1	4	4	
			3	1		8	Light brown
				1		10	
Triethanolamine.....	3	3	0	1	r	11	
			2	1	45 ^d	17	Purplish red

^a 70-30 brass unannealed, caliber .50 first draw pieces.

^b 70-30 brass unannealed cups.

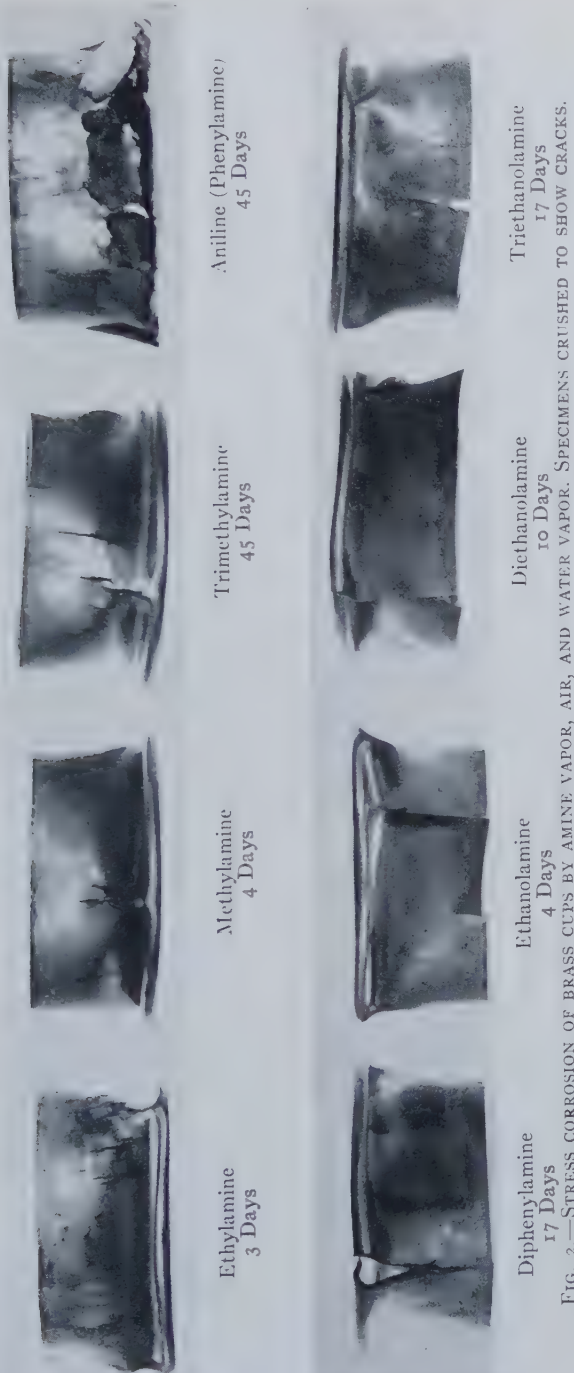
^r Test discontinued after 45 days exposure.

^s Test discontinued after 35 days exposure.

^d Found after pickling.

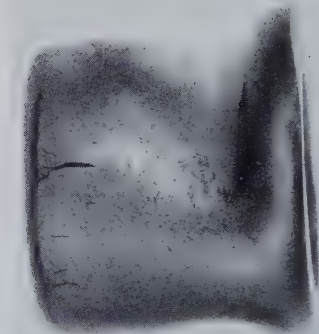
than 95 per cent diethanolamine. The triethanolamine was reported to contain not more than 2.5 per cent ethanolamine, not more than 15 per cent diethanolamine and not less than 80 per cent triethanolamine.

exposure and every third day thereafter until the exposures were discontinued at the end of 45 days. Specimens were withdrawn from the test after cracks had been detected.





Ethylamine
3 Days



Methylamine
4 Days



Trimethylamine
45 Days



Triethanolamine
45 Days



Ethanolamine
4 Days



Aniline (Phenylamine)
45 Days

FIG. 3.—STRESS CORROSION OF BRASS, CALIBER .50, FIRST DRAW PIECES (UNANNEALED) BY AMINE VAPOR, AIR, AND WATER VAPOR. SPECIMENS CRUSHED TO EXPOSE CRACKS.

Since the cracks in the cups usually opened wide, they were easily detected by visual examination. The draw pieces did not crack open to any appreciable extent, therefore a binocular microscope at a magnification of 20 diameters was used.

surface of the specimens became very dark.

RESULTS AND DISCUSSION

Cracking Data

A summary of the cracking results of the exposure tests is presented in Table 2.

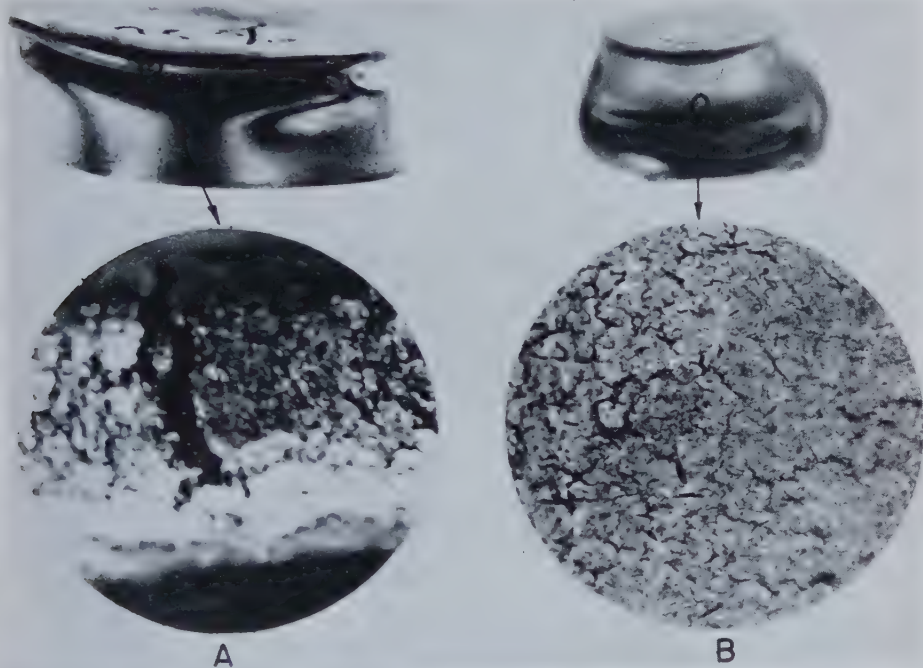


FIG. 4.—SURFACE CORROSION CAUSED BY THIRTY-MINUTE EXPOSURE OVER CONCENTRATED NH_4OH SOLUTION.

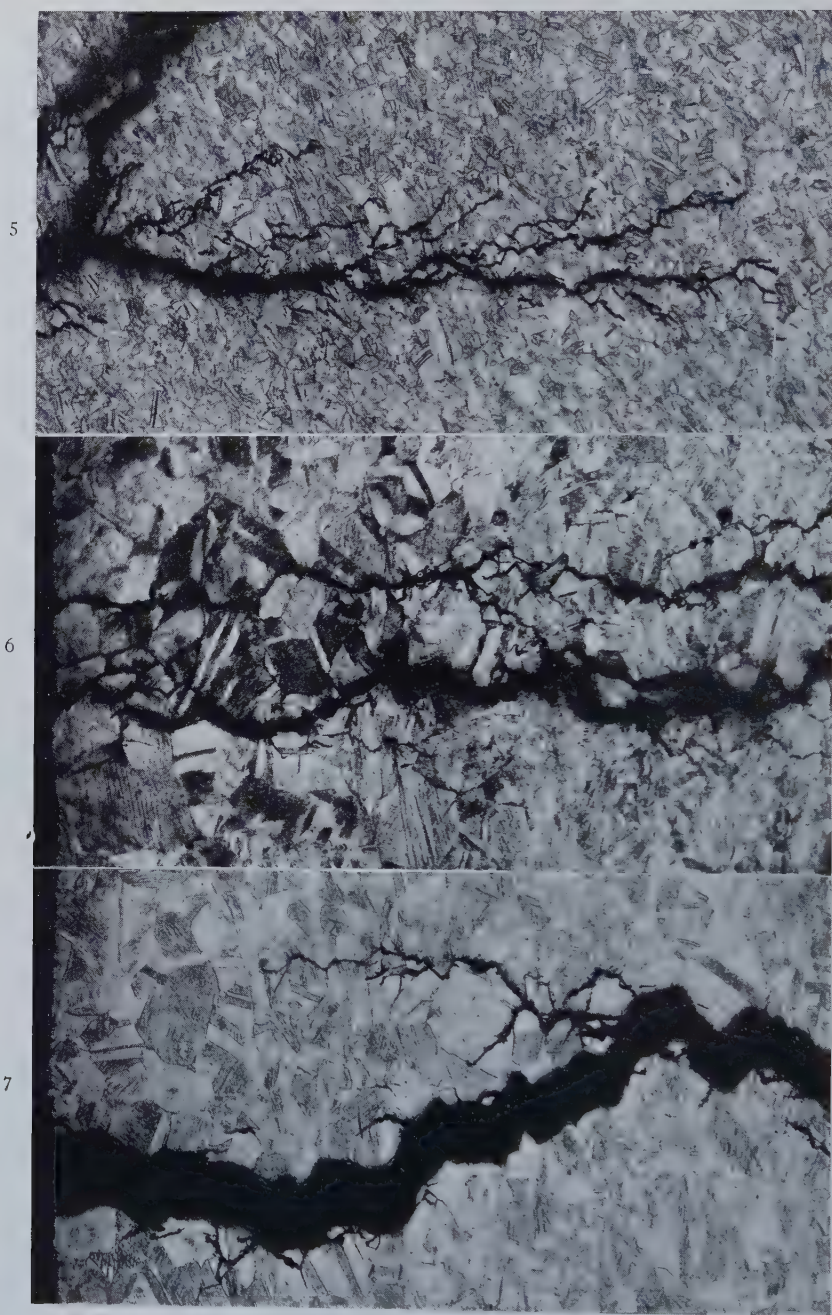
A, unannealed cup; B, unannealed caliber .50 first draw piece. Specimens shown natural size and surface at $\times 20$.

all remaining specimens were pickled to remove the corrosion products and examined at a magnification of 20 diameters. After being pickled in 10 per cent by volume H_2SO_4 (1.84 sp. gr.), several specimens were found to be cracked, although previous examinations had not disclosed small cracks assumed to have been hidden by the corrosion products.

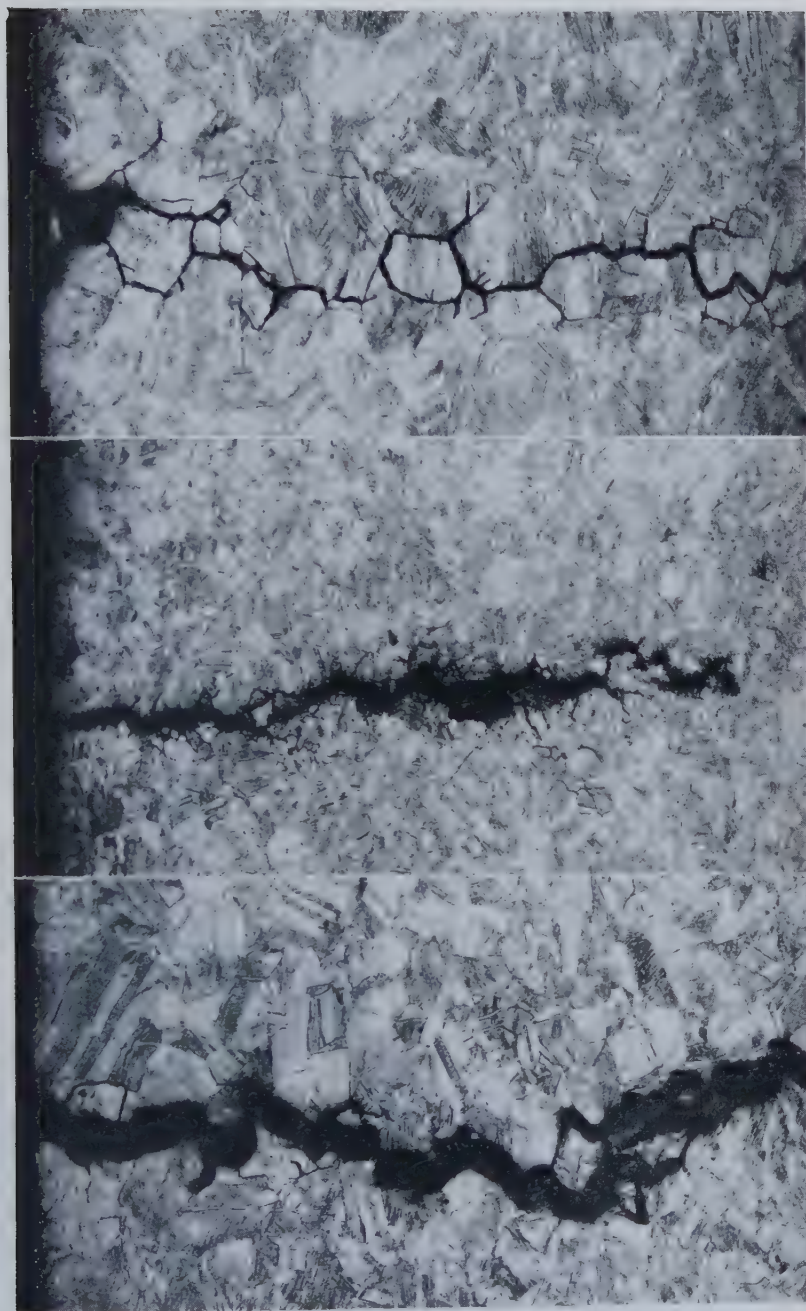
The color of the corrosion products was noted at the end of the first day of exposure. As the corrosion proceeded, the

Of the 13 amines tested, only three—diethylamine, triethylamine and pyridine—did not cause cracking. However, it is possible that higher concentrations of the amine vapor acting for an equal or greater length of time might have caused cracking. No cracking occurred among blank specimens in jars not containing amines.

No single series of amines appears to be harmless, since primary, secondary and tertiary amines have been shown to cause cracking.



FIGS. 5-7.—TRANSVERSE SECTIONS THROUGH BASE OF CALIBER .50 FIRST DRAW PIECES. ETCHANT:
 $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$.
5. Methylamine, 4 days.
6. Ethylamine, 3 days.
7. Trimethylamine, 45 days.
Original magnification 150; reduced $\frac{1}{4}$ in reproduction.



FIGS. 8-10.—TRANSVERSE SECTIONS THROUGH BASE OF CALIBER .50 FIRST DRAW PIECES. ETCHANT:
 $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$.

8. Aniline, 45 days.

9. Ethanolamine, 4 days.

10. Triethanolamine, 3 days.

Original magnification 150; reduced $\frac{1}{4}$ in reproduction.

On the basis of the available data, it is apparent that the primary amines are more active cracking agents than the secondary or tertiary amines in the methyl, ethyl, phenyl and ethanol series at the test temperatures used.

Macrostructure of the Cracks

The specimens were crushed so that the cracks became easily visible. Fig. 2 shows various cups and Fig. 3 shows various draw pieces that were exposed and afterward crushed.

The cup corroded by ethylamine shown in Fig. 2 is the most severely cracked and exhibits a type of surface deterioration similar to that obtained by ammoniacal atmospheres. This type of surface cracking is shown in Fig. 4, which illustrates a cup and draw piece exposed over a concentrated NH_4OH solution for $\frac{1}{2}$ hr. and afterward crushed. Large cracks have not developed, although the surface has a network of superficial cracks resembling fish scales; a specimen exposed to ammonia for a longer period of time develops larger cracks, similar to those in the ethylamine-corroded cup of Fig. 2.

Microstructure

The paths of all cracks examined were usually intercrystalline. Figs. 5 to 10 are photomicrographs showing cracks in draw pieces exposed to methylamine, ethylamine, triethylamine, aniline, ethanolamine and triethanolamine.

The plane of the microsection shown is a transverse plane cutting the intersection between the bottom and sidewall. The cracks are radial. A few branches of the main cracks go in other directions.

CONCLUSIONS

1. In the presence of moist air, amines can cause season cracking of stressed brass.
2. Under the conditions of these tests the primary amines are more active in

causing cracking than the secondary or tertiary amines.

ACKNOWLEDGMENTS

For permission to publish this paper, the authors are indebted to Lt. Col. C. H. Greenall, Officer in Charge of the Frankford Arsenal Ordnance Laboratory, and to the War Department, Office of the Chief of Ordnance. Appreciation is due Miss Reeder and Miss Miranshahian for help with the photographs and to Mr. H. Gisser and Mr. S. Spring for technical advice.

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DISCUSSION

(D. R. Hull presiding)

A. MORRIS,* Bridgeport, Conn.—I am not in any sense a student of organic chemistry, but I have been told that the amines are nitrogenous compounds that are capable of breaking down and producing small amounts, but appreciable ones, of ammonia; and inasmuch as ammonia is the only other source of cracking of this type that we know about, I have always had the suspicion that when amines cause cracks of this nature the real active agent may be ammonia still, rather than the amine itself.

I would like to know if the authors have made any tests to see whether small amounts of ammonia might have been present in those tests.

* Director of Research, Bridgeport Brass Co.

H. ROSENTHAL (author's reply).—I have no information about the decomposition of amines into ammonia during the test itself. However, some tests were made to determine whether any ammonia was originally present in the amines. It is very difficult to analyze for ammonia in the presence of amines because a test for ammonia generally turns out to be a test for amines as well.

The Francois test was found to be the best suited for the purpose, although even with this test only four of the amines could be

tested and the remainder of the amines yielded inconclusive results because of interference. The tests indicated that the ammonia content did not exceed 0.02 per cent in aniline, diphenylamine, triphenylamine and monethanolamine. Cracking was found with these four amines in the main tests. Experience has shown that ammonia contamination in the atmosphere from impurities in the order of 0.02 per cent will not produce the cracking observed in the testing of these four amines.

Physical Properties of a 65-Cu, 10-Mn, 25-Zn Alloy

By J. R. LONG* AND T. R. GRAHAM,* MEMBER A.I.M.E.

(New York Meeting, February 1944)

THIS report is concerned with part of a series of investigations carried on by the Federal Bureau of Mines on alloys, particularly nonferrous alloys, made with electrolytic manganese. A broad general program instituted after commercial quantities of electrolytic manganese became available was necessary in order to compare the effects of electrolytic manganese with those of the ordinary commercial grades. Representative analyses of these two materials show the commercial manganese metal to contain up to 2 per cent iron, a maximum of 1 per cent silicon and 0.06 per cent carbon, while the electrolytic manganese rarely exceeds 0.01 iron, 0.02 sulphur, with no silicon or aluminum.

In the literature, the emphasis has been largely on high-strength casting alloys containing up to 5 per cent manganese, and few data are available on wrought manganese alloys. These factors, coupled with the strategic position of copper and zinc, have given impetus to the Bureau's War Research Program for the development of alloys containing nonstrategic manganese for the purpose of supplementing or providing alternates for the more strategic metals. The alloy reported here was studied, along with several other ferrous and nonferrous

alloys, as possible cartridge-case material, and was chosen after a review of the properties of the ternary alloys of copper-manganese-zinc.

PRELIMINARY WORK

In a cursory survey of this system, alloys ranging from 60 to 95 per cent copper, 0 to 50 per cent manganese, and 5 to 40 per cent zinc were investigated. The alloys containing 60 per cent copper were found to fall into the two-phase alpha plus beta region of the system, and since those containing 70 per cent would not permit a saving, only alloys containing 65 per cent copper were considered. The tensile properties of these 65 per cent alloys are plotted in Fig. 1 as a function of manganese content for annealed material and for four conditions of cold-work. In the annealed condition the increases in strength and decreases in elongation are minor up to 15 per cent manganese; beyond this, the changes become more significant. In the cold-worked condition, the first 5 to 10 per cent of manganese appears to have the greatest strengthening effect, the rate of increase dropping off as the manganese increases beyond this amount. These effects are more pronounced with moderate than with severe cold reduction. It is also interesting to note that while the elongation of annealed material drops regularly with increasing manganese, the elongation in the cold-worked state is relatively little affected by increasing manganese content, particu-

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* Senior Metallurgists, Bureau of Mines, Intermountain Experiment Station, Salt Lake City, Utah.

larly beyond 20 per cent reduction by cold-rolling.

The 65 per cent copper, 10 per cent manganese, 25 per cent zinc alloy was

Fig. 2. These curves emphasize the close similarity of the properties of the manganese alloy to those of the brass upon cold-working and show that it is somewhat

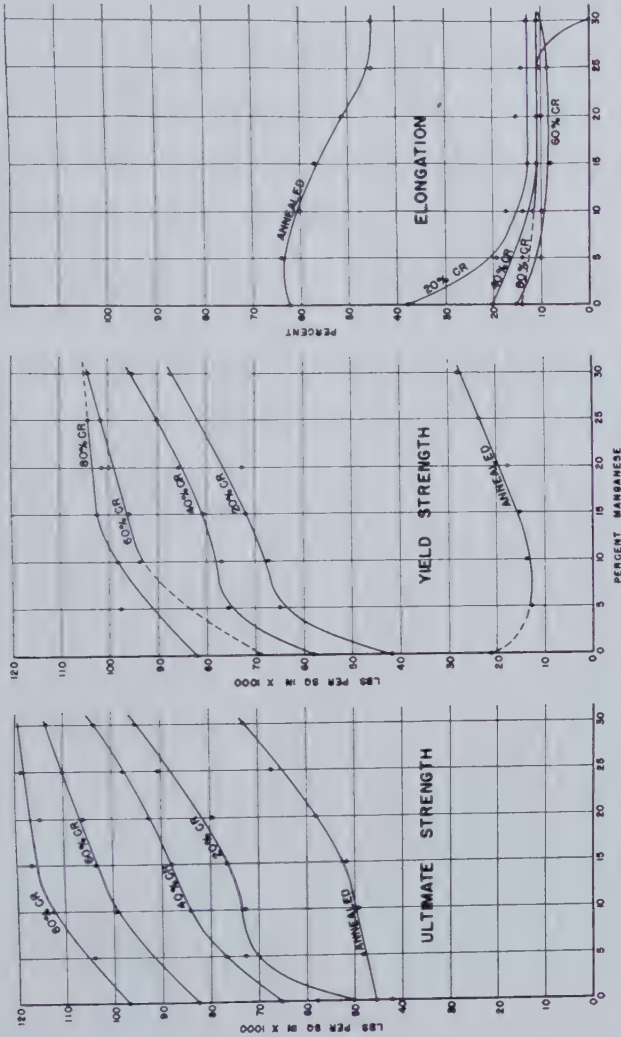


FIG. 1.—TENSILE PROPERTIES OF COPPER-MANGANESE-ZINC ALLOYS.
65 per cent Cu, 0 to 30 per cent Mn.

selected from these data because it contained the minimum amount of copper and zinc consistent with the possession of properties not too different from those of 70-30 brass. The properties of this alloy are compared with those of the brass in

stronger, a trifle harder, and has excellent ductility. The tensile and yield strengths do not exceed those of the brass by more than 5 to 8000 lb. per sq. in. in any condition; hardness is at most 5 points Rockwell B higher, and the percentage of elongation,

while 10 per cent less in the annealed condition, closely approaches that of the brass upon cold-working.

The relatively small divergence of

gravity 4 to 5 per cent lower than that of a cartridge brass, permitting a saving of copper and zinc over and above that obtained by simple weight substitution.

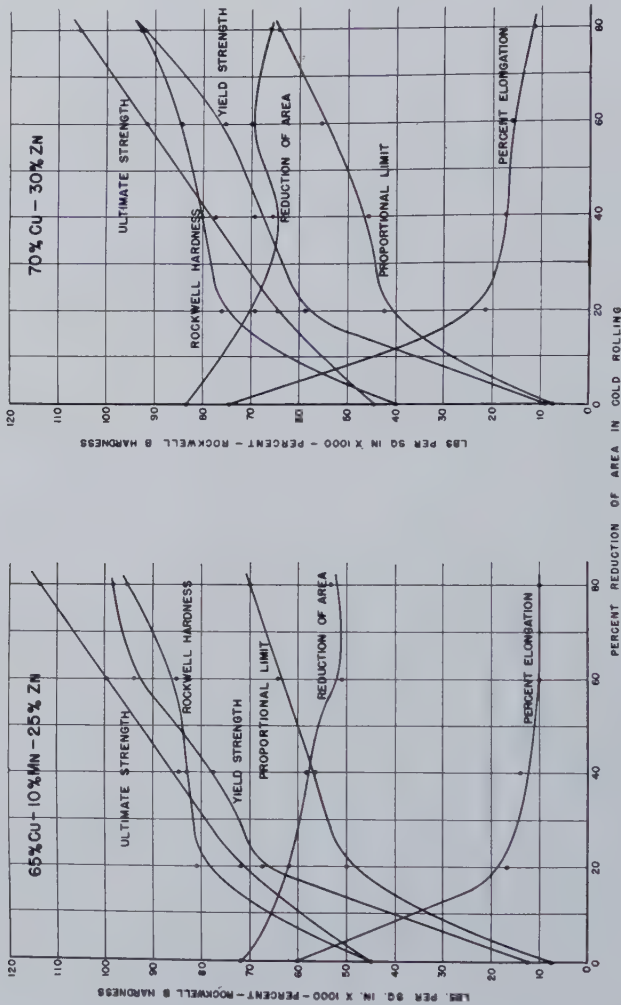


FIG. 2.—TENSILE PROPERTIES OF MANGANESE ALLOY COMPARED WITH ALPHA BRASS.

properties made it reasonable to expect that this alloy could be handled in much the same manner as 70-30 brass and could be utilized for cartridge cases and similar articles that demand good forming and deep-drawing characteristics, and thereby ease their requirements for badly needed copper and zinc. The alloy has a specific

Preliminary work was restricted to comparison of the properties of 70-30 brass with those of the electrolytic manganese alloy in rod form. Subsequent work was conducted to establish the properties of the manganese alloy when made with ordinary commercial metal as well as with the electrolytic manganese,

and to compare these with the properties of cartridge brass fabricated into sheet under identical conditions. Data were obtained on melting practice required to produce the alloy; hot-working and cold-working characteristics; variation of physical properties with cold-working and subsequent annealing; the effect of small variations in composition; microstructure and grain sizes; resistance to salt-spray corrosion; susceptibility to season cracking, and the effect of lead and antimony additions on hot-rolling characteristics.

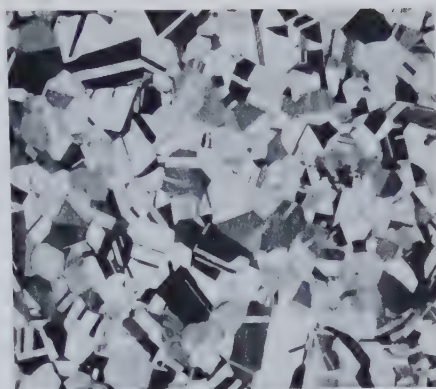
PREPARATION AND FABRICATION

The alloys were made from high-grade wirebar copper, electrolytic zinc, and two grades of manganese; that is, high-purity electrolytic cathode chips and ordinary commercial metal. While the melting and alloying were mostly carried out in high-frequency induction furnaces with magnesia or graphite crucibles, no difficulties have been encountered in making the

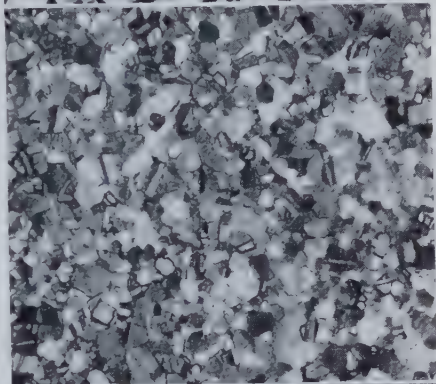
TABLE I.—*Chemical Analysis*
PER CENT

Alloy	Cu	Zn	Mn	Fe	Si	Al
1. Cartridge brass..	68.25	31.70	Nil	Nil	Nil	Nil
2. Electrolytic Mn..	65.00	24.90	10.05	Nil	Nil	Nil
3. Ordinary Mn....	65.00	24.45	10.30	0.27	Nil	Nil

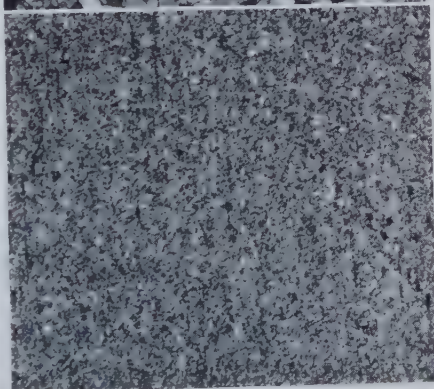
alloy in clay-graphite crucibles in a gas-fired furnace. The recommended melting procedure consists of first preparing a manganese-zinc hardener of the desired ratio (in this case 10-25) and adding the hardener to molten copper. Use of the hardener is a material aid in obtaining specific alloy compositions, and it is easily prepared by melting zinc under a sodium borate cover and gradually washing the manganese cathode chips into solution, using a copper-manganese stirring rod to push the manganese under the surface of the bath. Electrolytic manganese will dissolve in zinc with no serious difficulty up to 35 per cent, and the only precaution



3



4



5

FIGS. 3-5.—REPRESENTATIVE GRAIN SIZE OF ALLOYS PRIOR TO REDUCTION BY COLD-ROLLING. $\times 75$.

Fig. 3. Cartridge brass.

Fig. 4. Electromanganese alloy.

Fig. 5. Ordinary manganese alloy.

necessary is to keep the temperature below the flare point of the zinc. Ordinary manganese was more difficult to dissolve, and a considerably longer time was

required. These alloys have been made satisfactorily also by direct alloying and by using a copper-manganese hardener. However, the manganese-zinc hardener

All alloys were chill-cast into $1\frac{1}{2}$ by 3 by 19-in. slabs, which subsequently were machined to remove incidental surface imperfections. These slabs were hot-

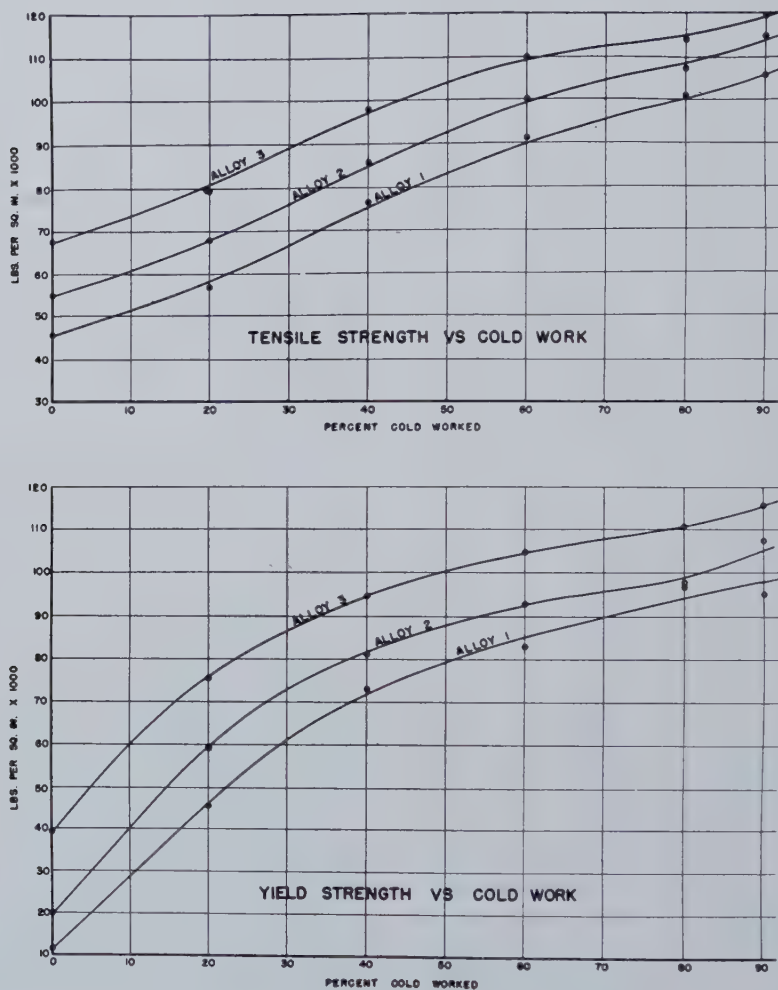


FIG. 6.—PROPERTIES OF ALLOYS 1, 2 AND 3 VS. COLD-WORK.

has the advantage of simplicity in preparation and good control of chemical composition, and requires only the single addition to molten copper to produce the alloy. These factors would be of particular importance in commercial preparation of the alloy. The chemical analyses of the alloys are reported in Table 1.

rolled and cold-rolled and annealed by schedules calculated to produce sheet finished to $\frac{1}{16}$ -in. thickness by various amounts of cold reduction. A hot-rolling temperature of 1300°F. (700°C.), found to be satisfactory in preliminary work, was used. The alloys hot-rolled quite well.

An annealing time of 30 min. at 1022°F. (550°C.) was used after tests on 60 per cent cold-reduced sheet showed that these conditions would not produce excessively

electromanganese alloy, these differences are not great. The ordinary manganese alloy has a much finer grain size, which persisted in all alloys made with ordinary

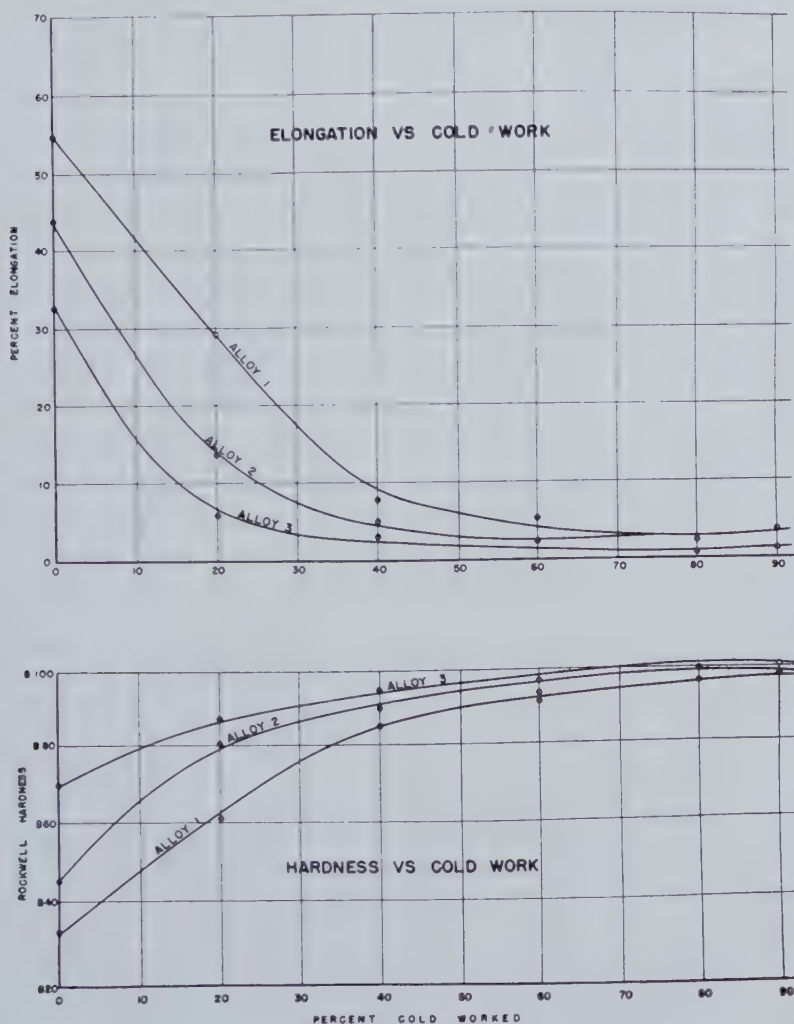


FIG. 7.—PROPERTIES OF ALLOYS 1, 2 AND 3 VS. COLD-WORK.

large grains in either the brass or the electrolytic manganese alloy. Representative annealed grain size of each of the three alloys prior to finish rolling are given in Figs. 3, 4 and 5. The photomicrographs show that while there are some differences between the grain size of the brass and the

manganese even when annealed at considerably higher temperatures.

Effect of Cold-rolling

The effects of plastic deformation by cold-rolling on the physical properties of the alloys are given in Table 2 and plotted

in Figs. 6 and 7 as a function of percentage of cold reduction. The work-hardening rates of the individual alloys from the standpoint of the tensile and yield-strength curves are strikingly parallel. It is to be noted in this comparison that each of the alloys 1, 2, and 3 has a different "as-annealed grain size," and that undoubtedly this accounts for at least part of the differences noted. The alloy made with ordinary manganese is definitely the hardest and has the highest tensile strength and lowest percentage of elongation, while the brass is softest and has the least strength and the highest elongation. The alloy made with electrolytic manganese is midway between the other two in all of its properties.

TABLE 2.—*Variation in Physical Properties with Cold-work*

AVERAGE OF THREE SPECIMENS

Alloy No.	Reduction in Thickness by Cold-rolling, Per Cent	Ultimate Strength, Lb. per Sq. In.	Yield Strength, Lb. per Sq. In.	Hardness, Rockwell B	Elongation, Per Cent
1	0	46,000	12,200	33	65
	20	57,200	46,500	61	29
	40	77,000	72,300	86	7.3
	60	91,000	83,000	92	6.4
	80	100,500	97,000	97	3.9
2	90	106,200	96,000	98	3.2
	0	55,000	20,300	45	43.5
	20	68,200	59,000	81	13.0
	40	85,500	81,500	90	4.6
	60	99,500	93,000	95	3.5
3	80	107,500	98,000	99	3.1
	90	114,600	107,300	101	3.5
	0	68,100	39,700	70	32
	20	69,200	75,500	87	7
	40	97,500	94,500	95	3.7
	60	110,000	104,500	98	3
	80	113,600	105,300	100	2.4
	90	119,000	116,000	102	2.8

The lower hardness and greater elongation of the electrolytic as compared with the ordinary manganese alloy makes it more desirable for purposes requiring high ductility for deep drawing. In addition, the closer approach of the tensile and yield strengths (8 to 10,000 per sq. in. higher) to those of the brass should make it easier to use this material interchangeably with

brass. The higher strength and lower elongation of the ordinary manganese alloy might be expected to introduce variation in procedure and results when fabricated by brass techniques. This was noticeable in the cold-rolling of the alloys, in that additional care was required to produce good sheet in the ordinary manganese alloy. It also offered more resistance to the reduction; that is, using the same roll setting and starting with the same initial thickness of metal, the brass and the electrolytic manganese alloy rolled to within half a thousandth of the same thickness while the ordinary manganese alloy was four thousandths thicker at a finished size of 80 thousandths of an inch.

Effect of Annealing Temperature

The variations of properties of the alloys with annealing temperature are given in

TABLE 3.—*Variation of Physical Properties with Annealing Temperatures*

AVERAGE OF THREE SPECIMENS

Alloy	Anneal Temperature, Deg. C.	Ultimate Strength, Lb. per Sq. In.	Yield Strength, Lb. per Sq. In.	Hardness, Rockwell B	Elongation, Per Cent
1	As rolled	91,000	83,000	92	6.4
	250	95,000	87,500	95	6.0
	350	56,600	28,200	56	50.0
	450	49,500	18,000	36	60.0
	550	46,000	12,200	33	65.0
2	650	43,000	9,000	53 ^F	75.0
	750	39,800	6,600	44 ^F	70.5
	As rolled	96,500	91,000	95	3.6
	250	97,100	90,500	96	4.2
	350	69,500	47,700	78	27.0
3	450	58,700	27,400	55	39.2
	550	55,000	20,600	47	44.0
	650	46,500	14,500	30	47.5
	750	45,600	12,900	60 ^F	51.0
	As rolled	104,000	96,000	98	3.0
	250	105,500	99,200	100	3.1
	350	98,000	89,500	97	5.8
	450	70,100	49,000	78	28.7
	550	68,100	39,700	70	32.0
	650	55,200	17,800	42	36.2
	750	49,800	13,100	31	40.0

Table 3 and Figs. 8 to 10. For this part of the work, test specimens of $\frac{1}{16}$ -in. sheet in the 60 per cent cold-reduced state were annealed for 30 min. at the indicated temperature and quenched in water. Through an oversight, none of the alloys was an-

nealed at 300°C. , which would correspond to the middle of the recrystallization range for brass and the beginning of recrystallization for the electrolytic manganese alloy.

and in the neighborhood of 250°C. for the brass. This is also reflected in the curves showing hardness and elongation plotted against temperature. Although the elonga-

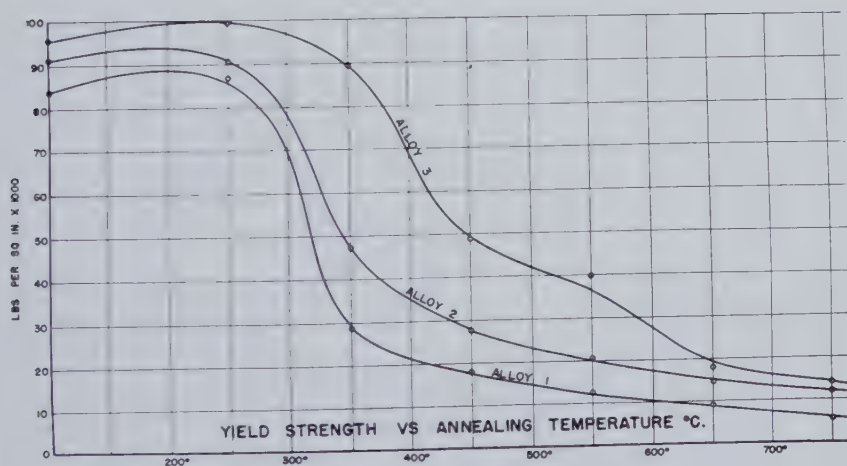
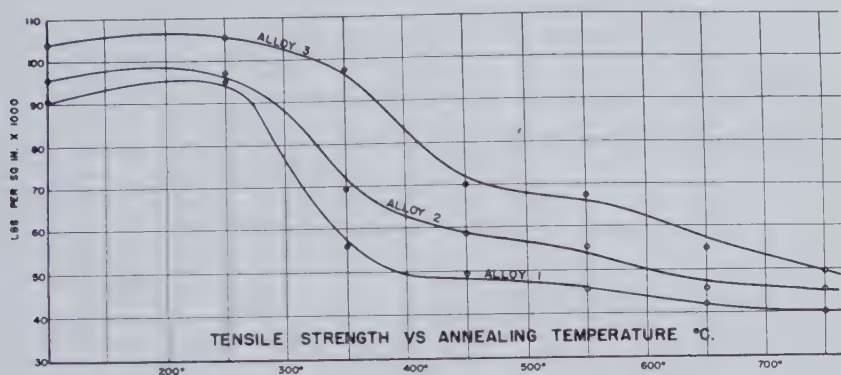


FIG. 8.—PROPERTIES OF ALLOYS 1, 2 AND 3 VS. ANNEALING TEMPERATURES.

The curves for the tensile and yield strength therefore are only approximate in this range, since they have been placed by rough approximation based on the hardness values given in Fig. 10.

It is evident from these data that the ordinary manganese alloy has the highest recrystallization temperature and that the recrystallization continues over a fairly wide range. Recrystallization begins at 300°C. for the electrolytic manganese alloy

and in the neighborhood of 250°C. for the brass. This is also reflected in the curves showing hardness and elongation plotted against temperature. Although the elonga-

tion of the electrolytic manganese alloy in the sheet form is below that of the brass, it is at least 10 per cent above that of the ordinary manganese alloy for all annealing temperatures.

The effect of annealing temperature on grain size is shown in Fig. 9, where it is evident that the grain size of the brass is the greatest of the three alloys and that the ordinary manganese alloy has the smallest grain size at all temperatures. Roughly, the

electrolytic alloy has a little more than half the grain size of the brass for all temperatures up to 700°C. At 800°C. the electrolytic alloy shows a decrease in grain

to 16, inclusive. The beginning of recrystallization is evident at 300°C. (Fig. 11), and complete at 420°C. (Fig. 12). The increase of grain size with temperature is illustrated

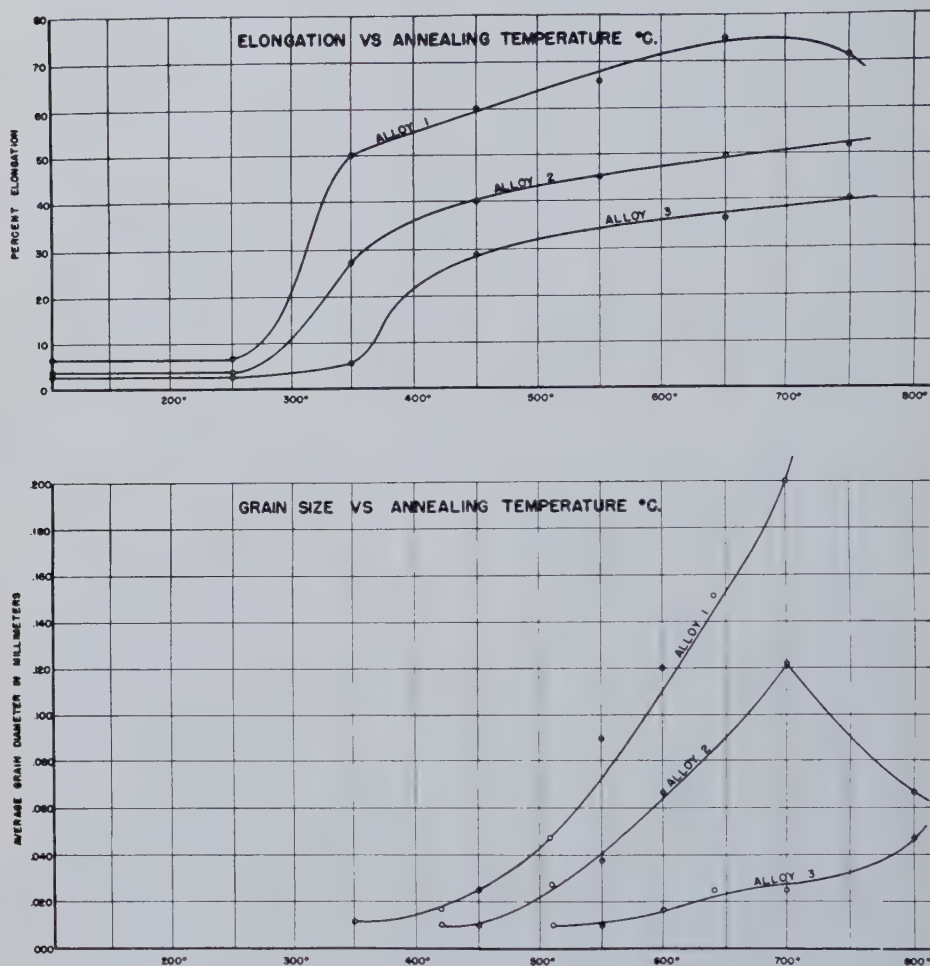


FIG. 9.—PROPERTIES OF ALLOYS 1, 2 AND 3 VS. ANNEALING TEMPERATURES.

size due to the formation of 10 to 15 per cent beta solid solution. The smaller grain size of the ordinary manganese alloy is due undoubtedly to its iron content, and is partly responsible for the greater hardness and strength and lower elongation exhibited in these results.

The grain sizes obtained on the electrolytic manganese alloy are shown in Figs. 11

by Figs. 12 to 15; Fig. 16 shows the beta constituent found at 800°C. in this alloy.

Effect of Variation in Composition

To determine the effect of small changes in chemical composition, a series of six alloys was made, varying about 2.5 per cent from the nominal 65 per cent copper, 10 per cent manganese, and 25 per cent zinc.

Microstructures and grain size were also studied for annealing temperatures from 250° to 800°C., to note the recrystallization

limits of the alpha solution area as affected by composition. The recrystallization temperatures, grain size, and amount

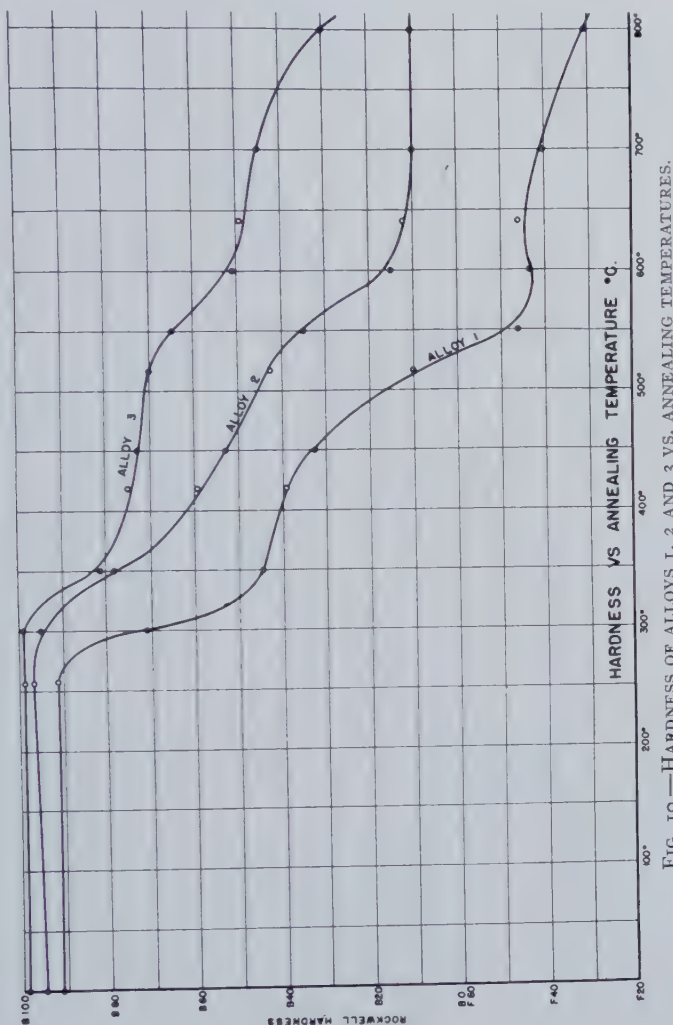


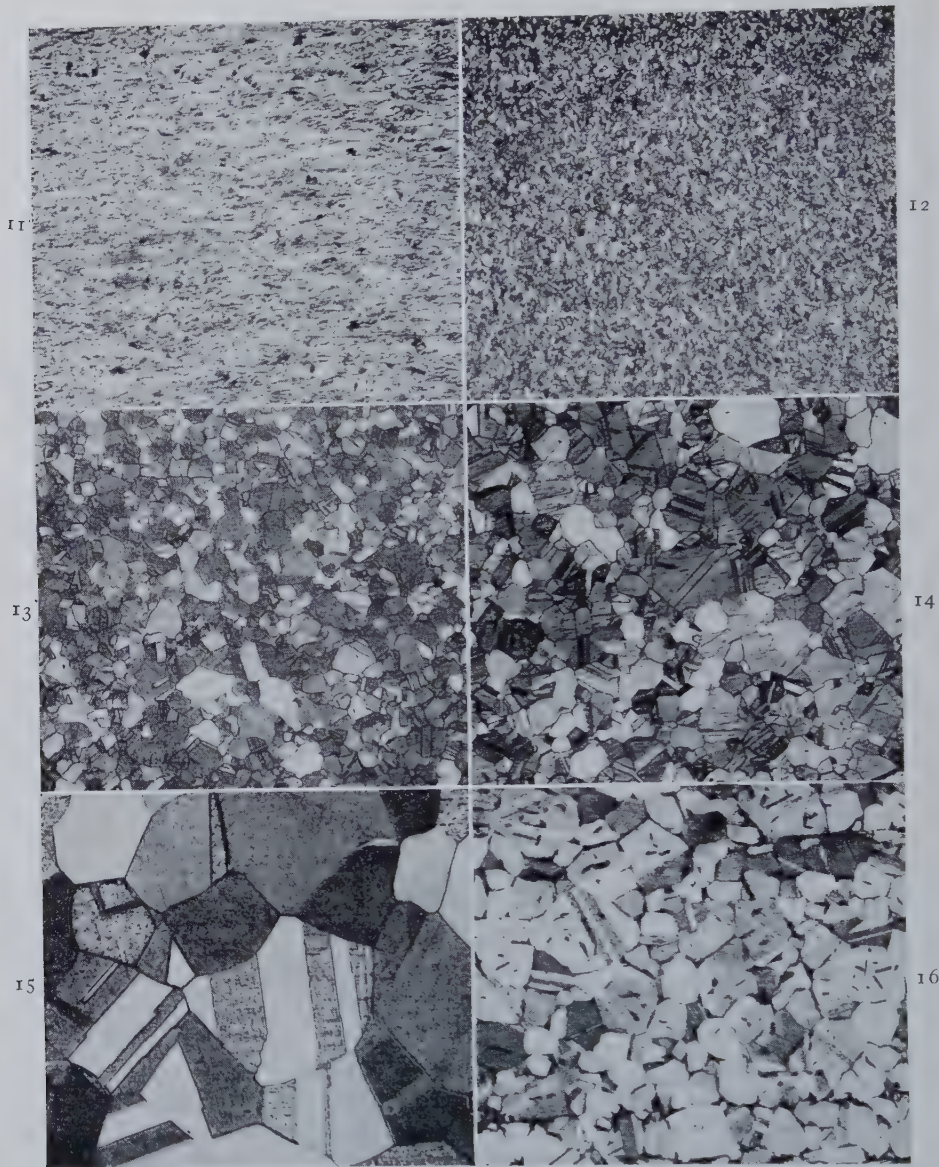
FIG. 10.—HARDNESS OF ALLOYS 1, 2 AND 3 VS. ANNEALING TEMPERATURES.

temperatures and also the temperature at which the beta phase was introduced.

While temperatures employed in fabrication were low enough to keep the basic alloy single phase, annealing-temperature studies indicated that the alpha plus beta field shifts toward the copper-manganese base line with increasing temperature. It was desirable therefore to determine the temper-

of the beta constituent found are presented in Table 4, and the shift of the alpha boundary is graphically represented in Fig. 17. In this graph the alpha plus beta boundary for copper-zinc alloys was taken from published data³ and extended to conform with the data in Table 4.

³ References are at the end of the paper.



FIGS. 11-16.—MICROSTRUCTURES OF 60 PER CENT COLD-WORKED ELECTROLYTIC MANGANESE ALLOY HEATED AT INDICATED TEMPERATURES FOR 30 MINUTES. $\times 150$.

Fig. 11. Annealed at 300°C.

Fig. 12. Annealed at 420°C.

Fig. 13. Annealed at 510°C.

Fig. 14. Annealed at 550°C.

Fig. 15. Annealed at 700°C.

Fig. 16. Annealed at 800°C.

For alloys with less than 64 per cent copper the beta constituent will be present at 64 per cent and over, and the working

versely, if the copper content is maintained at 64 per cent and over, and the working

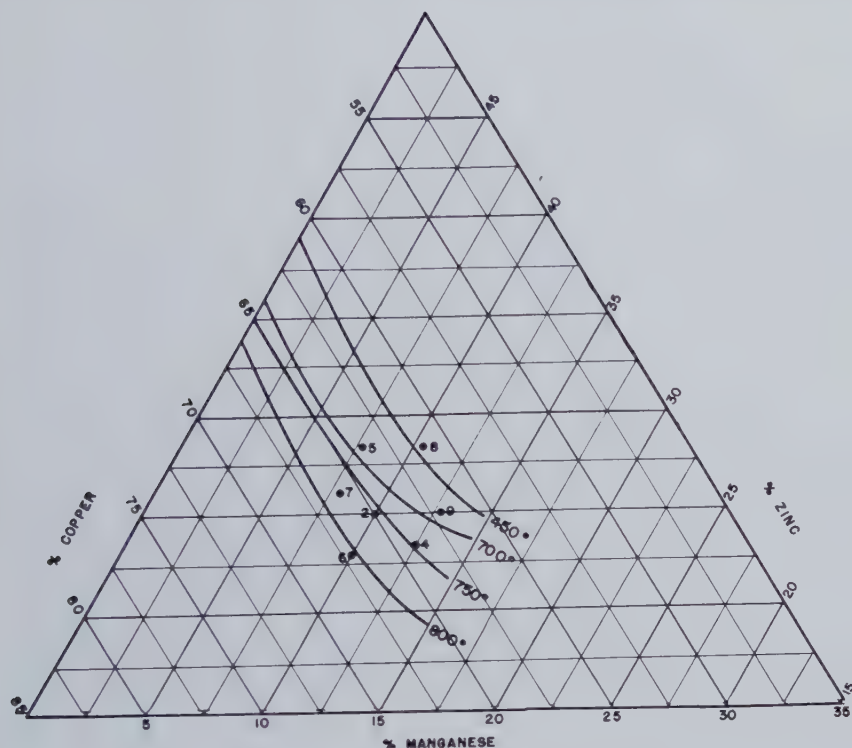


FIG. 17.—ISOTHERMS SHOWING BOUNDARY OF BETA-PHASE SEPARATION.

TABLE 4.—Structures and Grain Size Obtained by Heating to Indicated Temperatures
SPECIMENS OF 60 PER CENT COLD-REDUCED SHEET, HELD AT TEMPERATURE FOR 30 MINUTES

Alloy ^a	250°C.	300°C.	350°C.	400°C.	450°C.	500°C.	550°C.	600°C.	650°C.	700°C.	750°C.	800°C.
8	CW ^b	CW	CW	Rx	5B ^c 0.010	5B 0.015	5B 0.025	10B 0.030	20B 0.025	25B 0.015	50B 0.015	90B
5	CW	CW	CW	Rx	0.010	0.015	0.035	0.065	0.045 5B	0.035 20B	0.030 50B	50B
9	CW	CW	CW	Rx	Rx	0.015	0.030	0.045	0.035 1B	0.025 10B	0.025 25B	30B
4	CW	CW	CW	Rx	0.010	0.015	0.035	0.065	0.135	0.150	0.075 5B	0.035 10B
2	CW	CW	Rx	0.010	0.010	0.025	0.045	0.065	0.075	0.120	0.075 10B	0.045 10B
7	CW	CW	CW	Rx	Rx	0.015	0.035	0.065	0.090	0.120	0.150 1B	0.065 1B
6	CW	CW	CW	Rx	<0.010	0.015	0.035	0.065	0.120	0.150	0.200	0.120 >0.200

^a Alloy numbers correspond to compositions given in Table 5.

^b CW indicates cold-worked structure; Rx indicates recrystallization begun and not yet complete. Average grain diameter in millimeters.

^c B with its preceding figure indicates percentage of beta estimated to be present.

at temperatures above 700°C., and at 800°C. all alloys containing less than 66.5 per cent copper will contain beta. Con-

and annealing temperature kept below 700°C., the alloys will show only the single-phase alpha solid solution. The formation

TABLE 5.—*Effect of Variation in Chemical Composition on Physical Properties of 0.0625-inch Sheet*

AVERAGE OF THREE SPECIMENS

Alloy No.	Chemical Composition, Per Cent			60 Per Cent Cold-worked				Annealed ^a at 1022°F.			
	Cu	Mn	Zn	Tensile Strength, Lb. per Sq. In.	Yield Strength, Lb. per Sq. In.	Hardness, Rockwell B	Elongation, Per Cent	Tensile Strength, Lb. per Sq. In.	Yield Strength, Lb. per Sq. In.	Hardness, Rockwell B	Elongation, Per Cent
4	64.0	12.5	Bal.	101,000	94,000	96	3.0	63,000	26,500	48	41.5
2	65	10.05	Bal.	96,500	91,000	95	3.5	55,000	20,600	47	44
5	63.45	8.10	Bal.	101,000	88,000	96	4.1	58,000	24,000	46	49
6	67.0	10.00	Bal.	99,500	97,000	95	3.5	61,000	28,000	53	39.5
7	65.95	8.10	Bal.	103,000	93,000	95	3.9	58,000	24,500	46	46
8	61.1	10.45	Bal.	110,000	96,000	97	3.7	64,000	29,000	55	41
9	61.7	13.10	Bal.	105,000	98,000	97	3.7	64,000	29,500	54	40

^a 60 per cent cold-worked sheet, annealed 30 min. at 1022°F. (550°C.).

of small amounts of this beta phase does not, however, greatly affect the properties, as can be seen in Table 5. Prior to the cold-working and upon annealing, all alloys were heated to 550°C., and alloy No. 8 contained about 5 per cent beta at this temperature without showing any great difference in either the cold-worked or annealed properties. Furthermore, as will be seen later, the formation of the beta phase may be of some assistance in the hot-working of the alloys.

Differences in grain sizes for these alloys treated at the same temperatures are not excessive for temperatures under 600°C.; at 650° and 700°C. some irregularities are apparent, and it is to be noted that the grain size is small in all cases where the beta constituent is present but not predominant.

Tensile properties obtained on these alloys with varying compositions are given in Table 5 for the 60 per cent cold-worked and for annealed material. In general, the properties vary slightly and, as might be expected, the low-copper alloys are the strongest while the high-copper alloys have the lower strengths. The hardness and elongation of the cold-worked alloys are reasonably uniform in spite of differences in tensile and yield strength. In the annealed condition there is greater divergence in both hardness and

elongation. However, the variations in composition do not produce great differences in properties; therefore close control of chemical composition in commercial preparation of the alloys will not be required other than that necessary to avoid introduction of the beta solution in material to be severely cold-worked.

Salt-spray Tests

The tensile properties of alloys 1, 2, and 3 after exposure in a salt-spray chamber for 30 days at room temperature with a 5 per cent salt solution are given in Table 6. The tensile and yield strengths show very little change, but the percentage elongation suffered considerably. The last column of the table gives the loss in elongation obtained by comparison of the data with the values in Table 2. In general, the electrolytic manganese alloy suffered the least, the brass most, and the ordinary manganese alloy almost as much as the brass; that is, the loss in elongation on a percentage basis is most severe for the brass and the ordinary manganese alloy. This can be seen from consideration of the relatively high losses that occurred in the brass and the relatively low values of elongation originally possessed by the commercial manganese alloy. In an earlier series of tests based on loss in weight of samples exposed in the salt-spray chamber

for 6 weeks, there was very little or no difference between the brass and the electrolytic manganese alloy. These results indicate that the electrolytic manganese alloy is somewhat more resistant to salt-spray corrosion than the 70-30 brass.

TABLE 6.—*Tensile Properties of $\frac{1}{16}$ -inch Sheet after 30 Days Exposure to Salt Spray AVERAGE OF THREE SPECIMENS EXCEPT WHEN NOTED*

Alloy	Reduction in Thickness by Rolling	Tensile Strength, Lb. per Sq. In.	Yield Strength, Lb. per Sq. In.	Elongation, Per Cent	Elongation Decrease
1	0	44,500	13,000	57	18
	20	54,500	44,500	22	7
	40	72,500	67,500	5.6	1.7
	60	85,500	79,000	3.5	2.9
	80	100,500	92,000	3.0	0.9
	90	102,500	95,000	3.0	0.2
2	0	52,300	20,600	34.5	9.0
	20	65,500	57,000	10.5	2.5
	40	81,500	76,000	3.7	0.9
	60	94,000	89,000	3.2	0.3
	80	106,000	99,000	3.3	0.2
	90	110,000	102,000	2.7	0.8
3	0	63,100	37,600	24.5 ^a	8.0
	20	77,200	73,000	5.5	1.5
	40	94,400	90,000	2.6	0.9
	60	104,000	98,000	2.0 ^a	1.0
	80	108,000	102,500	2.5	0.1
	90	112,000	107,000	2.0	0.8

^a Average of two specimens.

Season Cracking

Comparisons were made between the brass and the electrolytic manganese alloy as to susceptibility to season cracking. After much experimentation the test method settled on consisted of bending strips of a standard size to the same deflection as a simple beam, immersing them in the usual^{4,5} mercurous nitrate solution, and noting the relative time required to produce cracking. Little or no differences were noted between these alloys in the 60 per cent cold-reduced, 20 per cent cold-reduced and the annealed conditions. In the course of this work it was noted that the 20 per cent cold-reduced material of both alloys was most susceptible under the conditions of test, accordingly several additional tests were conducted on material 20 per cent cold-reduced and heated to 300° and 350°C. for

1 hr. The result indicated that susceptibility of the brass was greatly reduced by the 300°C. treatment and that a 350°C. treatment was required for the electrolytic

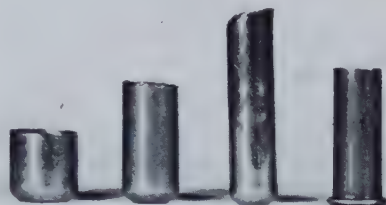


FIG. 18.—CUP AND SHELLS DRAWN FROM ELECTROLYTIC MANGANESE ALLOY.

manganese alloy to increase the cracking time to that of the brass treated at 300°C. From these tests it may be concluded that while the manganese alloy is susceptible to season cracking it is no more so than 70-30 brass.

Deep-drawing Test

Lack of equipment made it impossible to conduct extensive tests on the relative deep-drawing characteristics of these alloys when actually fabricated into cartridge cases. However, one trial of the electrolytic manganese alloy was made in which 0.015-in. sheet was blanked, cupped, and drawn into a shell and then headed in a manner similar to that used for rim-fired cartridge cases. The material was annealed prior to the blanking and cupping operation and then drawn and headed without any further heat-treatment. The test indicated that the material is capable of being worked in this manner at least as well as 70-30 brass. The successive stages of this deep-drawing test are shown in Fig. 18, which is a photograph of the cup, the two stages of drawing and the headed shell.

HOT-ROLLING BEHAVIOR

No difficulties were encountered in hot-rolling either the brass or the manganese alloys under the conditions used in the

experimental procedure of this investigation. However, Wilkins and Bunn,² among others, have reported poor hot-working characteristics of alpha brasses in the range 64 to 80 per cent copper and have stated that to hot-roll these alloys utmost care must be taken to maintain the lead content to a trace and that the presence of 0.03 per cent lead causes these alloys to fail by cracking at any hot-working temperature. The materials used in preparing these alloys contained only spectroscopic amounts of lead, and this no doubt accounts for the fact that the brass rolled very well in the fabrication of the alloys and in subsequent tests. Experiments were conducted to compare the hot-rolling characteristics of the lead-free brass and manganese alloys by determining the maximum reduction they would be capable of withstanding in a single pass without the development of surface or edge cracks. For the purpose, several pieces of alloys 1, 2, and 3, initially 0.800 in. thick, were heated at 1300°F. for 1 hr. and individual pieces hot-rolled with 15, 25, 35, 45 and 65 per cent reduction in thickness in a single pass. Each alloy withstood these reductions without the appearance of surface or edge cracking. This same procedure was also conducted on material with an original thickness of 0.425 in. Again the material withstood reductions up to 65 per cent in thickness in a single pass without failure of either the surfaces or edges; larger reductions were not attempted. From these tests it becomes apparent that no difficulty would be encountered in commercial processing of the alloys by hot-rolling.

Since fired small-arms cases eventually will find their way into brass production and may produce ingots containing 0.007 per cent antimony and 0.07 per cent lead, and Hull, Silliman, and Palmer⁶ have discussed the deleterious effects of these elements singly and together on the hot-working characteristics of brass, these studies were expanded subsequently to

include the effects of additions of lead and antimony to the alloys.

To observe these effects, alloys cast into tapered slab ingots were very carefully reduced by hot-rolling to a uniform thickness of 1 in., using small reductions (0.035 in. per pass) and numerous passes and returning the slabs to the furnace for a 15-min. period between passes. After the slabs were reduced to 1 in., they were given a minimum of 30 min. at the prescribed rolling temperature. Each slab was then rolled to give a reduction of $33\frac{1}{3}$ per cent in a single pass. The ability of the individual slabs to withstand this procedure without the development of surface or edge cracks was used as an index for satisfactory hot-rolling behavior. For the sake of simplicity, alloys containing ordinary manganese were omitted from this series. The percentages of lead and antimony as given are the amounts added and, considering the purity of the raw materials used, they are sufficiently accurate for the purpose. The results obtained on 16 heats of the cartridge brass and 33 heats of electrolytic manganese alloy are summarized below:

1. The manganese alloy containing lead could be successfully hot-rolled at 1500°F. with 0.14 per cent lead. As the rolling temperature was decreased the lead tolerance of the alloy also decreased and showed a limit of 0.07 per cent at 1400°F. and 0.04 per cent at 1300°F.

2. The manganese alloy containing 0.01 per cent antimony rolled satisfactorily at 1300°F.; higher percentages of antimony were not tested.

3. With antimony and lead together, hot-rolling was successful with a manganese alloy containing 0.10 per cent lead and 0.01 per cent antimony at a temperature of 1500°F. At 1400°F. this composition showed moderate general failure; at 1300°F. an addition of 0.05 per cent lead and 0.005 antimony was sufficient to produce moderate general failure, although at 1500°F. it could be rolled successfully.

4. The practical limit of lead in 70-30 brass was 0.02 per cent at a rolling temperature of 1450°F.

5. At 1450°F. it was possible to roll 70-30 brass with 0.01 per cent antimony; higher percentages of this element were not tested.

6. Cartridge-case brass hot-rolled at 1450°F. and containing 0.05 lead and 0.005 per cent antimony showed moderate general failure; the addition of 0.1 lead and 0.01 antimony showed severe general failure.

It is obvious that the manganese alloy can be hot-rolled with much higher lead contents than the brass, and that this tolerance for lead increases as the rolling temperature is increased. It is also evident that antimony present with the lead is less harmful to the hot-rolling behavior of this alloy. These factors will become more important as scrap contaminated with lead and antimony becomes more prevalent. The only immediate explanation available for the higher tolerance for these impurities is based on the 10 to 15 per cent beta phase known to be present in the alloy at these rolling temperatures. Wilkin and Bunn, among others, have suggested that the beta phase is capable of dissolving up to 1 per cent lead, and that this is the reason that alpha plus beta alloys containing lead may be successfully hot-worked.

SUMMARY

1. The physical properties of the alloy containing 65 per cent copper, 10 manganese, 25 zinc, made with electrolytic manganese are intermediate between those of the alloy made with ordinary manganese and the properties of 70-30 brass.

2. Upon exposure for 30 days in salt-spray chamber the electrolytic manganese alloy suffers the least loss in percentage elongation.

3. The rate of grain growth of the electrolytic manganese alloy is less than that of brass; its grain size is slightly more than

half that for brass annealed at the same temperatures. The ordinary manganese alloy shows an extremely fine grain size, which is attributed to the iron introduced with the manganese.

4. Variations of 2.5 per cent from the nominal composition of the electrolytic manganese alloy show definite but not extreme changes in physical properties.

5. The alpha boundary of alloys in this region of the copper-manganese-zinc system has been established. Isotherms of the boundary almost parallel the constant copper-concentration lines of the diagram and shift toward the copper corner with increasing temperature.

6. The alloy is subject to season cracking but no more so than the 70-30 brass.

7. The alloy was processed into a rim-fired cartridge case without intermediate annealing, using punches and dies normally employed for brass.

8. The tolerances of the alloy for lead in hot-rolling is greater than that of brass; the alloy containing 0.14 per cent lead may be successfully hot-rolled at 1500°F. compared with a limit of 0.02 per cent lead for the brass at 1450°F.

9. Lead and antimony together are more injurious to the hot-rolling characteristics of 70-30 brass than to those of the manganese alloy; alloys containing as much as 0.1 per cent lead and 0.01 antimony can be readily rolled at 1500°F.

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DISCUSSION

(C. L. Mantell *presiding*)

F. M. WALTERS, JR.,* Washington, D. C.—What is the Young's modulus for your 10 per cent manganese alloys in comparison with the 70-30 brass?

J. R. LONG.—I am sorry that I do not have the actual figures at hand, but it is in the same general range. We do not have extensometers required for an accurate determination of modulus and the values obtained varied considerably. Our results ranged from 13 to 17×10^6 lb. per sq. in. with similar values for the 70-30 brass. We thought the data a bit too variable to include here.

A. A. BATES,† East Pittsburgh, Pa.—In the section in which you compared the three alloys, one sees as the only apparent difference that of 0.25 per cent of iron. In the curves that compare the three alloys, it seems that the addition of 10 per cent of manganese gives a certain effect with regard to elongation, or hardness, or whatever criterion you may choose. The addition of about 0.25 per cent of iron practically doubles that effect. That seems rather strange. I should like to know whether there is an explanation for it—or is there a mysterious virtue of electrolytic manganese that brings that about?

J. R. LONG.—It is perhaps a mysterious attribute of the ordinary manganese that brings it about. We believe that the differences are largely due to the differences between the two raw materials.

A. A. BATES.—Differences other than the iron that is shown?

J. R. LONG.—Yes, the differences in the iron content shown and differences of silicon content that are not shown. In other words, analyses show silicon "Nil," meaning under 0.05; the other alloys also showed silicon under 0.05, so that while there is no apparent difference an actual difference can exist.

A. A. BATES.—How about differences in such elements as hydrogen, oxygen, and so forth? Do you expect anything there?

J. R. LONG.—Nitrogen might have a decided effect. Some of the other work we have done shows it has a powerful effect. I would hesitate at this time to attribute these differences, however, to nitrogen alone. I would prefer to attribute it to the impurities as a whole rather than to any one.

MEMBER.—Was there a difference in the aluminum content of the two supplies of manganese?

J. R. LONG.—There is a difference in the aluminum content of two raw materials. This is what I was going to say before. The ordinary manganese, of course, is more impure than the electrolytic manganese and contains iron, silicon and aluminum and carbon. The only one that showed up in these analyses was the iron. I would hesitate to blame it all on the iron, although a good part of it may be due to it.

As far as the aluminum content of the finished alloys is concerned, they were all under 0.025. We used some aluminum as a deoxidant for the alloys, but they were all under 0.025 in the finish.

A. A. BATES.—In view of the relative similarity of the iron and manganese atoms, it seems rather startling to say that 25 per cent iron is making all that vast difference on top of the 10 per cent of manganese.

J. R. LONG.—If you blame it partly on the grain size and admit that the iron is partly controlling grain size, I think you can come fairly close to the answer. The iron is not particularly soluble in the alloy, whereas the manganese is. That is another point of difference.

C. O. THIEME,* Chicago, Ill.—You mentioned that silicon was present on the order of 0.05 to 0.5 per cent. Is that correct?

J. R. LONG.—Not quite. Let me say that 0.05 is a maximum. It was not present in excess of that.

* Naval Research Laboratory, Anacostia Station.

† Research Laboratories, Westinghouse Electric and Manufacturing Company.

* Works Manager, H. Kramer and Company.

C. O. THIEME.—You mentioned that there was 0.025 maximum aluminum. One of the major differences between electrolytic and ferro grades of manganese is sulphur. A complete analysis—unless you are order bound or cannot give the information on account of war conditions—will probably show the reason for the great difference in the two grades of manganese, will it not?

J. R. LONG.—Such analytical information as we have has not been too satisfactory. Determination of manganese in this alloy is not simple. Determination of aluminum, lead, and carbon have not been very consistent. The chemical laboratory has worked rather hard at it, but I think it has been too rushed with a number of other things to really give it the attention required.

I am not trying to say that you cannot get these analyses, but we did not consider them sufficiently important to make a great effort to get them, which would have been necessary in order to get the information you are asking for.

We have attached no importance to the 0.02 per cent sulphur in the manganese and we have attached no importance to the aluminum content. We have added aluminum in deoxidizing the alloys and were satisfied when the laboratory reported under 0.025.

Likewise, on the lead the information reported in the paper is on the basis of added lead rather than as analyzed. It is very difficult to separate lead and manganese in the analytical procedures and the results that we have obtained on the procedures used have not been entirely satisfactory. In other words, I cannot

give you the information you ask for because our analytical work was not carried to that extent. We did not feel it was necessary to justify the work it would entail.

C. O. THIEME.—The reason I bring those questions up is simply because of the fact that in rolling-mill practice it has been my understanding that a very small percentage of impurities affects the properties of 70-30 brass. We also know that in the manufacture of high-strength casting alloys—that is, a high-strength manganese bronze—we have been able to secure higher elongations by using electrolytic manganese.

I call your attention to the fact that these small amounts of impurities are important and the additive effect must not be overlooked.

J. R. LONG.—The points raised by Mr. Bates and Mr. Thieme concerning the effect of the impurities in the ordinary manganese may perhaps best be answered by the statement that we believe that the differences noted between the alloy made with electrolytic manganese and that made with ordinary manganese are due entirely to the impurities present in the ordinary manganese. These same differences have also been observed in other alloys that we have examined and we believe them to be due largely to iron and silicon, most likely affecting the properties through a control of the grain size of the alloy. The ordinary manganese is also contaminated by oxides and nitrides and these may play an additional part, but since we have few experimental data concerning them we cannot say much about them at this time.

The Constitution of the Lead-antimony and Lead-antimony-silver Systems

By B. BLUMENTHAL*

(Chicago Meeting, October 1943)

THE LEAD-ANTIMONY SYSTEM

THE present investigation was planned as a survey of the lead-rich portion of the ternary lead-antimony-silver system by thermal analysis. Since, however, a rigorous application of the conventional thermal analytical method is time consuming, an attempt was made to speed up the investigation by reducing the time required for a single thermal analysis. This was done by increasing the rate of cooling to 12° to $18^{\circ}\text{C. per minute}$. Since such a rate does not permit even an approach to equilibrium conditions, the melt was stirred vigorously by a stirrer operating at the high rate of 665 r.p.m. This proved to be effective in obtaining cooling curves with distinct points of arrest and of excellent reproducibility, which satisfactorily compare with those obtained at a rate of 1° to $2^{\circ}\text{C. per min.}$ with or without slow stirring (Fig. 1).

By this method the lead-rich end of the lead-antimony system and a series of ternary alloys in sections parallel to the lead-antimony side of the ternary system were investigated and it was observed that the two branches of the liquidus curve of the binary alloys did not intersect at the eutectic temperature. An equivalent effect was observed in the ternary system.

The eutectic temperature of the binary lead-antimony system was found to be 252.0°C. , which confirms the recent in-

vestigation by Pellini and Rhines,¹ who determined the eutectic temperature to be 251.5°C.

The observation that the curves of primary crystallization of the lead-antimony system do not intersect at the eutectic temperature was previously made by Dean.² Dean explains the phenomenon by assuming the existence of a compound Sb_4Pb . He felt that supercooling was not the cause of the phenomena because he was unable to influence them by inoculation.

The X-ray investigation by Solomon and Morris-Jones,³ the metallographic investigations by Stead,⁴ Charpy,⁵ Gontermann,⁶ and Dean, Zickrick and Nix,⁷ and the numerous investigations of physical properties, definitely disprove the occurrence of any compound.

The work of Dean was not confirmed by Broniewski and Sliwoski,⁸ whose experiments did not show any irregularity and who report a eutectic composition of 13 per cent antimony and a eutectic temperature of 250° to 252°C. at a rate of cooling of about $6^{\circ}\text{C. per min.}$ Abel, Redlich and Adler⁹ then report a eutectic composition of 12.1 per cent upon reviewing the previous publications and adding a few of their own cooling curves. In 1934 Quadrat and Jiříš¹⁰ found from careful analyses of the bottom portion of slowly cooled hypereutectic melts that the eutectic contains only 11.4 to 11.5 per cent antimony. (Previous analyses by Stead⁴ in 1891 gave 13 per cent.) Weaver,¹¹ however, reported in 1935 that cooling curves indi-

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* Research Metallurgist, Central Research Laboratory, American Smelting and Refining Co., Barber, N. J.

¹ References are at the end of the paper.

cated the eutectic composition as being nearer 12.7 per cent than 13 per cent, without giving any experimental data. In 1939 Seltz and DeWitt¹² determined the eutectic composition to be 12.1 per cent.

All these discrepancies apparently are accentuated by stirring and cooling rates, and it was suspected that they are produced by supercooling. It was felt that an investigation of the effect of stirring and rate of cooling on the crystallization temperatures would solve the problem.

Methods

The alloys were made from Perth Amboy refined lead and pure antimony. Some alloys were prepared from lead and antimony of high purity: the lead containing as only impurities, bismuth 0.0002 per cent, copper 0.0001 per cent; the antimony, only lead <0.0005 per cent. The alloys were prepared in clay-graphite crucibles, or in a Pyrex beaker over a gas burner by melting the lead and dissolving the antimony at about 400° to 500°C. At first no flux was used. This is entirely satisfactory for alloys up to 10 per cent antimony, since with skillful operation the loss of antimony due to oxidation is negligible. The loss by oxidation in preparing alloys with more than 10 per cent antimony was about 0.1 to 0.2 per cent. The high-purity alloys were prepared under a cover of high-flash-point tempering oil without loss of antimony due to oxidation.

The rapid rate of cooling of 12° to 18°C. per min. was obtained by placing a small clay-graphite crucible containing about 500 grams of molten metal in a larger crucible, which was preheated to 125°C., and covering each crucible with asbestos sheet. A medium rate of cooling of about 5°C. per min. was obtained by filling the space between the two crucibles with infusorial earth and preheating both the outer crucible and the insulating material to 125°C. The slowest rate of cooling was obtained by placing a 50-c.c. Pyrex beaker

containing 300 grams of metal in a large graphite crucible, then putting both in a

TABLE 1.—Results of Thermal Analyses of Lead-antimony Alloys at Various Rates of Cooling

No.	Anti- mony Content, Per Cent	Rate of Cooling ^a Deg. C. per Min.	Grade ^b	Liquidus Tem- pera- ture, Deg. C.	Eutectic Tem- perature
HYPOEUTECTIC ALLOYS					
F-846	3.15	1.6	H.P.	304.5	(243.5) ^d
F-774	5.0	18.0	R	292.4	(247.2) ^e
F-845	6.3	0.9	H.P.	283.9	N.D. ^f
F-845	6.3	0.8 ^g	H.P.	285.9	N.D.
F-845	6.3	0.6 ^g	H.P.	285.4	N.D.
F-819	9.1	1.6	R	265.6	252.1
F-756	9.8	13.8	R	259.4	251.8
F-852	10.1	1.0	H.P.	259.1	251.7
F-812	10.9	12.6	R		252.6
HYPEREUTECTIC ALLOYS RAPIDLY COOLED					
F-813	11.8	12.7	R		252.3
F-814	12.7	12.7	R	256.4	252.3
F-815	13.5	13.8	R	264.3	251.7
F-816	15.3	15.0	R	283.8	252.5
F-853	15.5	14.1	R	282.1	251.3
F-855	15.5	13.6	R	284.5	252.8
HYPEREUTECTIC ALLOYS COOLED AT MEDIUM RATE					
F-814	12.7	5.2	R	259.5	252.3
HYPEREUTECTIC ALLOYS SLOWLY COOLED					
F-849	12.6	1.1	H.P.	259.6	252.0
F-818	12.7	1.3	R	262.4	251.1
F-848	13.3	1.0	H.P.	270.5	N.D.
F-820	13.5	1.6	R	270.1	251.7
F-847	15.3	1.4	H.P.	286.0	251.1
F-847	15.3	1.0	H.P.	285.4	N.D.
F-847	15.3	0.7 ^g	H.P.	286.3	N.D.
F-847	15.3	1.5 ^g	H.P.	286.3	253.0
F-847	15.3	1.5 ^g	H.P.	289.5	N.D.
F-853	15.5	0.9	R	291.0	N.D.
NONSTIRRED ALLOYS					
F-756	9.8	17.1	R	256.7	247.7
F-754	14.5	15.4	R	258.1	249.3
F-753	15.5	14.5	R	269.6	249.3

^a Taken from the slope of the cooling curve shortly before reaching the liquidus temperature.

^b H.P., alloys of high purity; R, alloys of regular purity.

^c Rate of heating.

^d Small effect due to incomplete equilibrium.

^e Since most of the alloy is solid at this temperature the melt could not be stirred.

^f N.D., not determined.

well-insulated electric pot furnace with all interspaces filled with infusorial earth and covering the furnace carefully with an

asbestos sheet. The melt was covered with high-flash-point oil. Unless otherwise noted all melts were vigorously stirred by an electrically driven Pyrex stirrer at 665 revolutions per minute.

tained the equilibrium temperature of the melt did not introduce an error, some temperature measurements were made by means of an unprotected Chromel-Alumel thermocouple and a potentiometer. The

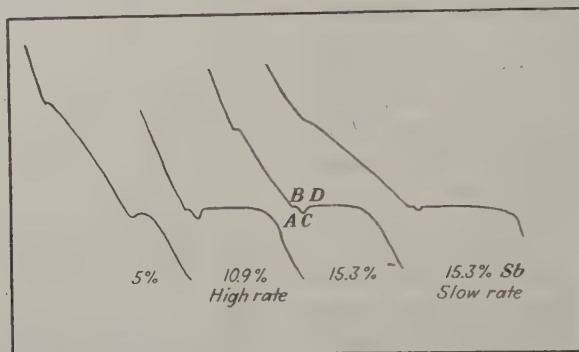


FIG. 1.—COOLING CURVES OF LEAD-ANTIMONY ALLOYS.

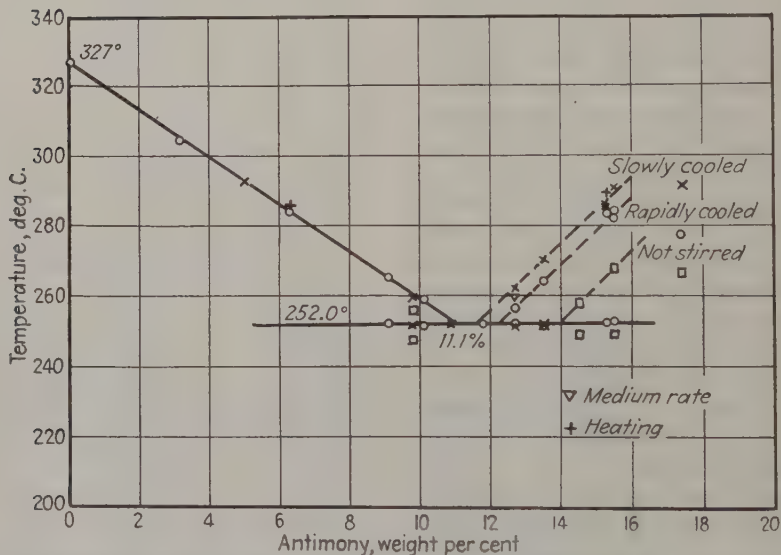


FIG. 2.—LIQUIDUS AND EUTECTIC TEMPERATURES OF LEAD-ANTIMONY ALLOYS FOR VARIOUS CONDITIONS.

The temperatures were measured by a gas-filled mercury thermometer calibrated under the conditions of the experiments against the melting points of Perth Amboy lead and pure tin with the accepted melting temperatures of 327°C. and 232°C., respectively. To make sure that the time that elapsed before the thermometer at-

results of these measurements were the same as those obtained by the mercury thermometer within the error of the experiment. Readings were made in intervals of 10 sec. at rapid cooling or 1 min. at slow cooling. The error of the single temperature measurement was within $\pm 0.5^\circ\text{C}$. The liquidus and eutectic temperatures are

considered to be correct within $\pm 1^\circ\text{C}$. Most of the specimens were analyzed. Their composition is correct within ± 0.1 per cent.

Typical cooling curves at various rates are shown in Fig. 1.

Data

The results of the thermal analyses for various conditions are shown in Table 1 and Fig. 2.

The rate of cooling has no influence on the liquidus temperatures of the primary lead crystallization. The points of all alloys except the points of the nonstirred alloys are found on a straight line.*

The picture is different on the side of the primary antimony crystallization. Here, the liquidus temperatures are higher the lower the cooling rate, and the liquidus temperatures are lowest, if the melts are not stirred. Apparently, the true liquidus temperatures were never reached.

The eutectic temperature is 252.0°C ., which is the average of all experiments in which the melt could be stirred at the eutectic temperature. Nonstirred alloys show the lower eutectic temperatures as reported by previous investigators. The temperature of 252.0°C . may be regarded as the true eutectic temperature, since variation of the cooling rate does not affect it if the melt is stirred.

As it is well known that antimony metal is susceptible to supercooling, the phenomena observed apparently are supercooling phenomena. Vigorous stirring and a slow rate of cooling are not sufficient to completely counteract the tendency to supercool. It is surprising that even inoculation of a nonstirred melt such as attempted by Dean has no influence.

The results of a few heating curves are included in Table 1. The temperatures obtained from the heating curves are about 1° to 2° higher than those obtained from the cooling curves. Since the accuracy of these experiments was somewhat less on heating than on cooling, less weight is attached to the results of the heating curves than to those of the cooling curves.

As the gap between the liquidus curves is still 0.5 per cent even if the melts are vigorously stirred and slowly cooled, it must be concluded that the true eutectic point is found at the intersection of the liquidus curve of the primary lead crystallization with the eutectic temperature of 252.0°C . This point is at 11.1 per cent antimony.

If only the alloys up to 11.1 per cent antimony are considered, the curve of primary lead crystallization as given in Fig. 2 is in close agreement with the results of most of the previous investigators.^{2,6,8,13-15,17} This is shown in Fig. 3, which also contains the solidus curve by Pellini and Rhines¹ and the boundary of the alpha solid solution by Obinata and Schmid.¹⁶

Since the apparent temperature of the primary antimony crystallization depends on the rate of cooling, it is possible to extrapolate the data graphically for various rates of cooling at constant concentration to infinitely slow cooling and thus approximately determine the true temperature of primary crystallization for each concentration. The curve of the primary antimony crystallization in Fig. 3 is the result of this extrapolation to infinitely slow cooling (see Table 2).

Effect at Initial Stage of Eutectic Crystallization

The beginning of crystallization of the lead-antimony eutectic is accompanied in a number of cases by a special effect. As the temperature of the melt decreases the crystallization starts at the anticipated

* The linear function: $t = -675.6x + 327$, in which t is the temperature in degrees Centigrade and x the antimony content in weight per cent, represents the results extremely well. This also covers the alloys of low antimony concentration investigated by Heycock and Neville.¹⁷

eutectic temperature (point *A* in Fig. 1) but soon stops (point *B*). Subsequently, the melt continues to cool and supercool to point *C* and then the eutectic crystallizes

both rates are extremely small. Some nuclei are already present when the eutectic temperature is reached. These nuclei grow slowly, producing a small thermal effect,

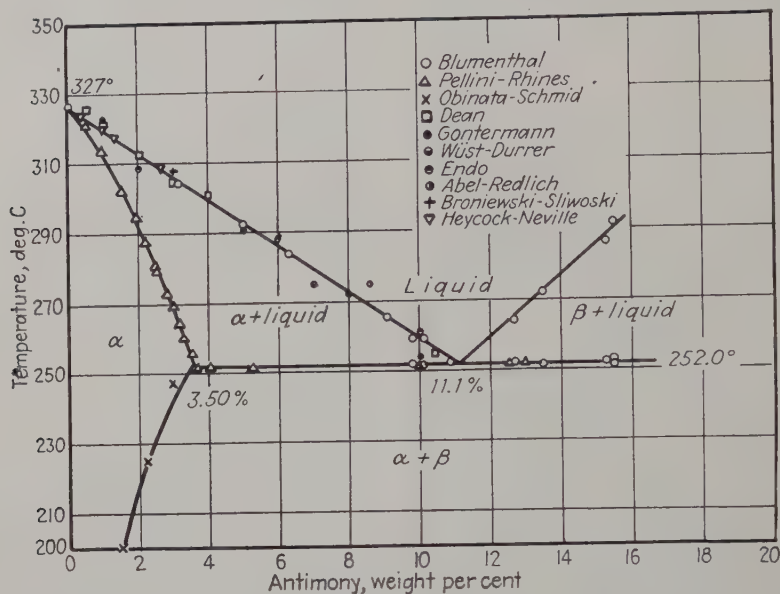


FIG. 3.—CONSTITUTIONAL DIAGRAM OF LEAD-RICH LEAD-ANTIMONY ALLOYS.

in the way usually observed on supercooled melts. The temperature shoots up (to point *D*) until heat equilibrium is reached.

TABLE 2.—*Liquidus Temperatures of Some Hypereutectic Lead-antimony Alloys*
VALUES EXTRAPOLATED TO INFINITELY SLOW COOLING

ANTIMONY CONTENT, WEIGHT, PER CENT	LIQUIDUS TEMPERATURE, DEG. C.
12.7	264
13.5	272
15.3	286.5
15.5	292

The effect (*A-B*) that takes place preliminary to supercooling at the initial stage of the eutectic crystallization occurs on melts of high as well as regular purity, on hypoeutectic and hypereutectic alloys, and was observed at all rates of cooling in stirred alloys regardless of the methods of temperature measurement.

The effect may be explained in terms of rate of nucleation and rate of growth. It is assumed that at the eutectic temperature

which, however, is not great enough to compensate for the heat loss of the total system. Since the rate of nucleation is small, crystallization of the melt and liberation of the latent heat depends entirely on the slow growth of the few nuclei originally present in the melt. This will continue until the temperature of the melt is low enough to ensure the formation of a sizable number of nuclei, which then bring about the regular eutectic crystallization.

THE LEAD-ANTIMONY-SILVER SYSTEM

The constitution of the lead-antimony-silver system has not been previously investigated. The only publication is by Guertler,¹⁸ who predicts the existence of a quasibinary system between lead and the compound Ag_3Sb . Since, however, two of the boundary systems (Pb-Sb and Pb-Ag) are eutectiferous and the third one (Ag-Sb) forms two peritectics and one eutectic, it

was suspected that the liquidus surface of the ternary system has two transition binary alloys.¹⁹ The lead-rich end of the lead-antimony system was changed accord-

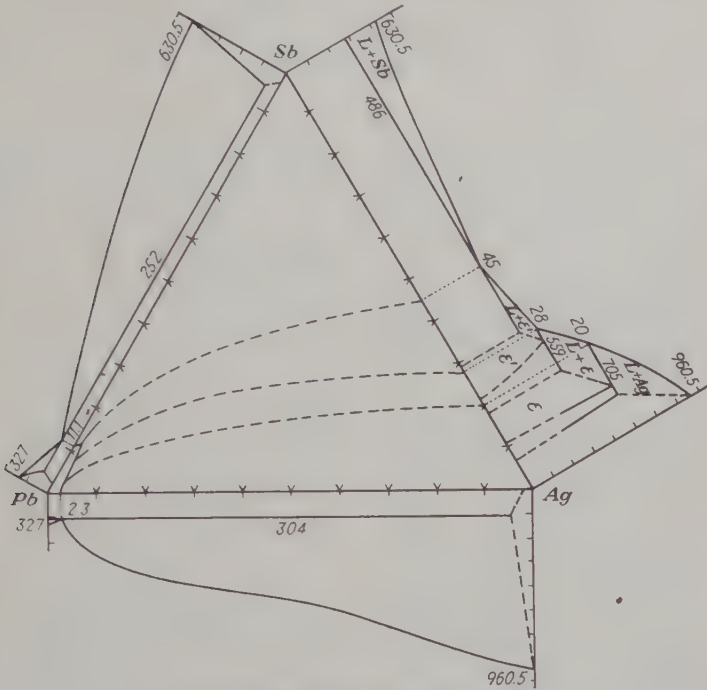


FIG. 4.—SCHEME OF LIQUIDUS SURFACE.

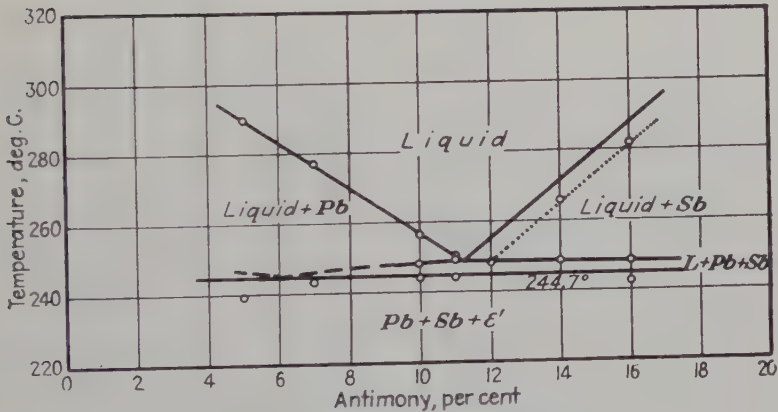


FIG. 5.—SECTION AT 0.4 PER CENT SILVER PARALLEL LEAD-ANTIMONY. Dotted lines indicate result of supercooling.

points in addition to a eutectic one. The scheme of such a system is shown in Fig. 4. The three boundary systems were taken from Hansen's book on the constitution of

ing to the results of the first section of this paper.

The lead-rich corner of the system was investigated by the rapid thermal analysis

described above. The rate of cooling was 12° to 18°C. per min. and the rate of stirring 625 r.p.m. The alloys were prepared from

TABLE 3.—*Results of Thermal Analysis of Lead-antimony-silver Alloys at High Rate of Cooling*

Specimen No.	Composition, Per Cent			Liquidus Temperature, Deg. C.	Intermediate Arrest, Deg. C.	Solidus Temperature, Deg. C.
	Ag	Sb	Pb			
F-768	0.4	5.0	94.6	289.9		239.7 ^a
F-807	0.4	7.0	92.6	277.3		243.2 ^a
F-762	0.4	10.0	89.6	256.6	248.3	244.2
F-808	0.4	11.0	88.6	250.6	249.6	244.2
F-804	0.4	12.0	87.6	248.3 ^a		Not distinct
F-805	0.4	14.0	85.6	265.5 ^a	248.6	Not distinct
F-806	0.4	16.0	83.6	281.8 ^a	248.4	242.2
F-769	0.8	5.0	94.2	286.3	254.3	240.5 ^a
F-809	0.8	7.0	92.2	273.9	250.3	241.1 ^a
F-763	0.8	10.0	89.2	254.3	245.2	243.7 ^a
F-810	0.8	11.0	88.2	248.3	246.2	244.2
F-786	0.8	12.0	87.2	246.2 ^a		244.2
F-787	0.8	14.0	85.2	261.5 ^a	247.2	245.0
F-788	0.8	16.0	83.2	278.9 ^a	247.2	245.0
F-789	0.8	18.0	81.2	295.2 ^a	247.2	244.7
F-831	2.0	3.0	95.0	291.9		239.3 ^a
F-772	2.0	5.0	93.0	287.3	281.2	240.1 ^a
F-832	2.0	6.0	92.0	284.2	276.5	241.5 ^a
F-790	2.0	7.0	91.0	277.6	268.6	241.1 ^a
F-791	2.0	8.0	90.0	276.2	264.5	241.5 ^a
F-792	2.0	9.0	89.0	277.3	259.2	243.3 ^a
F-833	2.0	9.0	89.0	276.2	259.0	243.2 ^a
F-834	2.0	10.0	88.0	274.9	252.8	245.2
F-758	2.0	12.0	86.0	271.1		244.7
F-779	2.0	14.0	84.0	265.3	258.7	244.4
F-790	2.0	16.0	82.0	270.8 ^a	264.5	244.4
F-781	2.0	18.0	80.0	289.1 ^a	268.9	244.7
F-803	3.0	1.0	96.0	325.4	301	
F-802	3.0	2.0	95.0	327.4	297.2	237.1 ^a
F-801	3.0	3.0	94.0	326.4	292.9	238.6 ^a
F-797	3.0	4.0	93.0	322.9	288.4	239.9 ^a
F-835	3.0	4.0	93.0	324.5	288.9	240.1 ^a
F-773	3.0	5.0	92.0	324.7	282.8	240.1 ^a
F-796	3.0	6.0	91.0	322.4	277.8	240.9 ^a
F-799	3.0	7.0	90.0	320.8	272.6	241.6 ^a
F-795	3.0	8.0	89.0	317.8	266.8	242.0 ^a
F-798	3.0	9.0	88.0	314.2	261.2	243.3 ^a
F-759	3.0	10.0	87.0	307.1	254.3	244.2 ^a
F-782	3.0	12.0	85.0	306.6	259.7 ^a	244.8
F-783	3.0	14.0	83.0	303.1	256.7 ^a	244.8
F-784	3.0	16.0	81.0	297.8	272.2 ^a	244.7
F-785	3.0	18.0	79.0	291.9	288.3	244.8
F-811	3.0	20.0	77.0	299.2 ^a	294.1	244.7
F-770	1.2	5.0	93.8	283.7	273.7	240.2 ^a
F-771	1.6	5.0	93.4	280.1	278.4	240.1 ^a
F-777	4.0	5.0	91.0	345.4	284.7	239.7 ^a
F-765	1.15	10.0	88.85	252.1		244.4
F-766	1.4	10.0	88.6	250.2	249.2	244.2
F-767	1.6	10.0	88.4	256.8	252.2	244.2
F-761	4.0	10.0	86.0	337.8	255.8	244.2

^a Supercooled.

Perth Amboy lead, fine silver and pure antimony in clay-graphite crucibles by melting the lead, dissolving the silver in

the lead and then adding the antimony. Enough analyses were made to confirm the nominal composition of the alloys within ± 0.2 per cent. The thermometric temperature measurements were correct within $\pm 1^\circ\text{C}$.

TABLE 4.—*Location and Temperatures of the Eutectic and Transition Curves in the Lead-antimony-silver System*

Curve or Point	Composition, Per Cent			Temperature, Deg. C.
	Ag	Sb	Pb	
FE	0	11.1	88.9	252.0
	0.4	11.2	88.4	249
	0.8	11.3	87.9	247
GE	3.0	18.4	78.6	290
	2.0	15.0	83.0	262
	1.8	14.0	84.2	259
HE	1.4	12.0	86.6	249
	2.3	0	97.7	304
	1.7	5.0	93.3	279
IT ^a	1.5	10.0	88.5	250
	3.0	10.0	87.0	307
	2.0	7.0	91.0	277
JT	3.0	4.0	93.0	324
	1.4	11.4	87.2	244.7
	1.7	6.0	92.3	272
E	2.1	1.5	96.4	297
T ^b				

^a Approximate data.

^b Estimated.

Data

The following sections through the ternary system were investigated:

1. Section at 0.4 per cent Ag parallel Pb-Sb.
2. Section at 0.8 per cent Ag parallel Pb-Sb.
3. Section at 2.0 per cent Ag parallel Pb-Sb.
4. Section at 3.0 per cent Ag parallel Pb-Sb.
5. Section at 5.0 per cent Sb parallel Pb-Ag.
6. Section at 10.0 per cent Sb parallel Pb-Ag.

The results of the thermal analyses are shown in Figs. 5 to 10 and Tables 3 and 4. The system follows the general pattern shown in Fig. 4.

The same supercooling phenomena with respect to the antimony crystallization that were observed in the binary system were also found in the ternary system. Supercooling takes place first at the primary

antimony crystallization, second at the secondary antimony crystallization if no primary antimony crystallization is preceding, third at the eutectic crystallization if

result of supercooling, are denoted by dotting.

The liquidus surface of the lead-rich corner of the system is shown in Fig. 11.

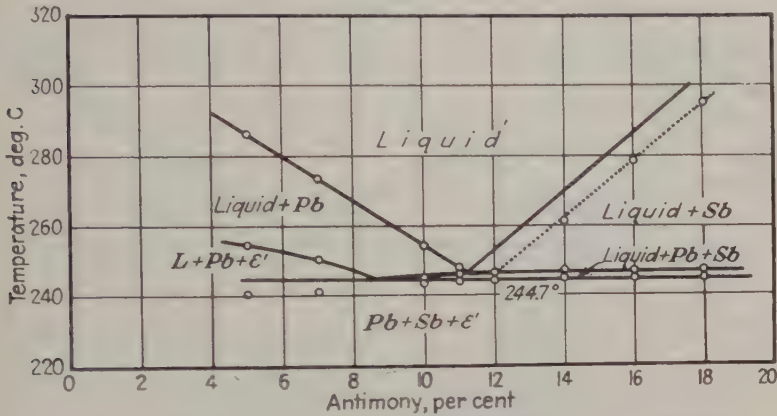


FIG. 6.—SECTION AT 0.8 PER CENT SILVER PARALLEL LEAD-ANTIMONY. Dotted lines indicate result of supercooling.

no primary or secondary antimony crystallization is preceding or if the amount of eutectic in the alloy is so small that the partly frozen melt cannot be stirred. Also,

The eutectic (point *E*) consisting of lead, antimony and ϵ' solid solutions contains 11.4 per cent Sb, 1.4 per cent Ag and 87.2 per cent Pb; it freezes at 244.7°C. Primary

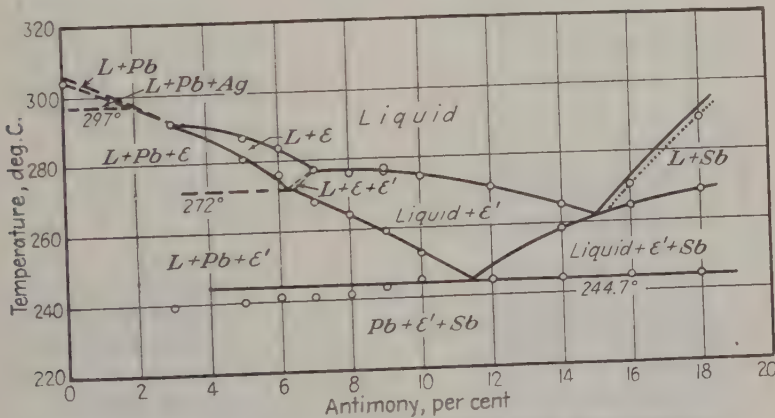


FIG. 7.—SECTION AT 2.0 PER CENT SILVER PARALLEL LEAD-ANTIMONY. Dotted lines indicate result of supercooling.

the delaying effect observed at the initial stage of the eutectic crystallization of the lead-antimony alloys was found in the ternary system. The temperature-concentration curves in Figs. 5 to 9, which are the

crystallization of lead solid solution takes place in field $PbFET'THPb$. Primary antimony solid solution crystallizes above FEG . The curves JT and TH limit the primary crystallization of the silver solid

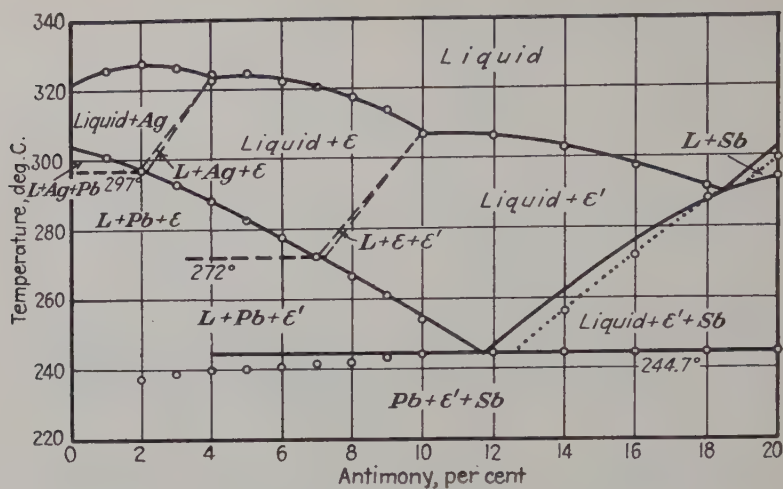


FIG. 8.—SECTION AT 3.0 PER CENT SILVER PARALLEL LEAD-ANTIMONY. Dotted lines indicate result of supercooling.

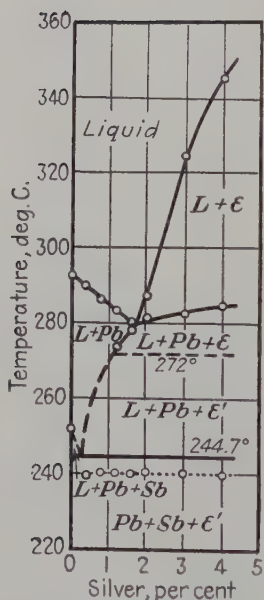


FIG. 9.—SECTION AT 5.0 PER CENT ANTIMONY PARALLEL LEAD-SILVER. Dotted lines indicate result of supercooling.

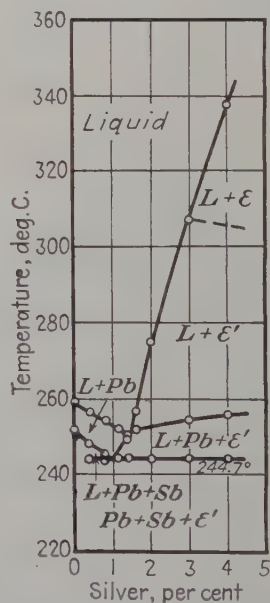
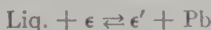


FIG. 10.—SECTION AT 10.0 PER CENT ANTIMONY PARALLEL LEAD-SILVER.

solution. The boundary of the primary crystallization of the ϵ phase is $IT'TJ$ and that of the ϵ' phase is $GET'I$. At the secondary eutectic crystallization along the curve HE the lead and silver phases crystallize in section HT , the lead and ϵ phases in section TT' and the lead and ϵ' phases in section $T'E$.

The invariant equilibrium



occurs at the temperature T' . Another invariant equilibrium



was assumed to exist at the temperature T .

Both reactions are suppressed by the great rate of cooling employed and no thermal arrests related to these reactions are found on the cooling curves; therefore location and temperature of the transition point T' were determined by the intersection of the curve IT' with the secondary eutectic curve HE . The composition of the alloy T' is approximately 6.0 per cent Sb, 1.7 per cent Ag and 92.3 per cent Pb. The transition temperature is about 272°C . Location and temperature of point T could only be estimated since only one point of the curve JT was determined. They should be close to 1.5 per cent Sb, 2.1 per cent Ag, 96.4 per cent Pb and 297°C .

SUMMARY

The crystallization temperatures of the lead-rich lead-antimony alloys were re-determined by thermal analysis at various rates of cooling by experiments in which the melts were vigorously stirred.

The eutectic temperature was found to be 252.0°C .; the eutectic composition 11.1 per cent Sb and 88.9 per cent Pb.

The liquidus temperatures of the hypoeutectic alloys are not affected by the rate of cooling. The hypereutectic alloys supercool readily, depending on the rate of cooling. The supercooling effect is partially

removed by vigorous stirring at a slow rate of cooling.

A new effect observed on cooling curves at the initial stage of the eutectic crystal-

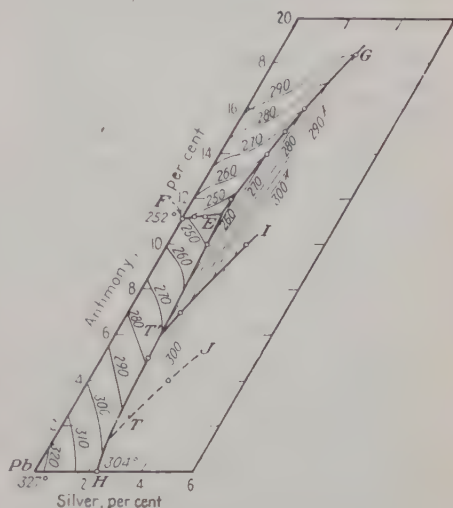


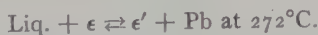
FIG. 11.—LIQUIDUS SURFACE.

lization is described and explained by coincidence of a slow rate of nucleation and slow rate of growth.

The liquidus surface of the lead-antimony-silver system in the neighborhood of the lead-rich lead-antimony alloys has been determined.

The system has a ternary eutectic of 11.4 per cent Sb, 1.4 per cent Ag and 87.2 per cent Pb at $244.7 \pm 0.5^\circ\text{C}$.

The invariant equilibrium



was deduced from experimental and theoretical evidence.

Another invariant equilibrium



was assumed to exist at a temperature of 297°C .

The same supercooling phenomena with respect to the antimony crystallization that were observed in the binary lead-antimony system were found to occur also in the ternary system.

ACKNOWLEDGMENT

The author wishes to express his thanks to the American Smelting and Refining Co. for permission to publish this work. He is greatly indebted to Dr. A. J. Phillips, Superintendent, Central Research Laboratory, American Smelting and Refining Co., and to Mr. A. A. Smith, Jr., under whose direction this work was done, for continuous collaboration and interest. Thanks are expressed to Dr. M. Eisemann and Mr. R. P. Yeck for the chemical analyses, and to Dr. R. D. McLellan for the spectrographic analyses.

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DISCUSSION

(E. E. Schumacher, presiding)

E. E. SCHUMACHER,* Murray Hill, N. J.—My associates and I have been interested in

* Bell Telephone Laboratories.

the lead-antimony alloy system for many years and have encountered supercooling in such alloys on many occasions. It has always been difficult for us to envisage how this phenomenon can occur in melts of hypoeutectic alloys in which a multitude of crystallites are present prior to the time the eutectic temperature is reached. Pre-eutectic formed crystals would be expected to provide nuclei on which both alpha and beta crystallites would readily precipitate. Apparently, however, the alpha crystallites have little effect in initiating precipitation of beta, and vice versa; consequently the supercooling. The data presented by Pellini and Rhines and by the present author are convincing in placing the eutectic at about 252°C. It should be borne in mind that in practical operations involving the melting of the lead-antimony eutectic a temperature less than 252°C. will almost always be encountered.

I should like to know whether the thermometer calibrations were made at the rapid rate of cooling and stirring. It would be interesting also to know the lengths of time that the melts were held at the eutectic temperature. A description of the stirrer should be given, since specifying speed alone does not permit one to gauge the degree of agitation occurring in the melt. The inclusion of microscopic data pertaining to the ternary would be valuable.

F. N. RHINES,* Pittsburgh, Pa.—The author is to be complimented on his successful suppression of undercooling in the very troublesome lead-antimony system. Although the method of stirring is a classic one, it has too often been overlooked in recent years. It is gratifying also to have confirmation of the eutectic temperature which Mr. Pellini and I published with some trepidation in view of the weight of other published evidence in favor of a lower value.

I should like to take this opportunity to suggest once again the advantages of using isothermal (horizontal) sections in the presentation of ternary diagrams. It is understandable that the metallurgist, being accustomed to temperature-concentration diagrams in the

* Department of Metallurgy, Carnegie Institute of Technology.

representation of binary equilibria, should want ternary diagrams to look the same. Vertical sections through the ternary space diagram are, indeed, somewhat similar to binary diagrams in their appearance, but there the resemblance ceases. The construction and interpretation of vertical sections involves pitfalls into which most of us blunder with discouraging regularity. In fact, the precautions that must be taken to avoid these traps are such that it is simpler on the whole to discard vertical sections altogether and to use isotherms exclusively. To illustrate this point I will mention a few of the more common difficulties.

Vertical sections usually are complicated both with regard to the number of equilibria represented and with regard to the forms of the boundary lines. It is almost impossible to ascertain the validity of a given construction, within the rules of thermodynamics, without first developing the corresponding isotherms. For this reason many fundamental errors of construction have been committed and the diagrams so effected can be shown to be impossible. Had isotherms been employed the mistakes would have been so evident that it is improbable that they would have been overlooked by their authors. No such errors are apparent in the present paper.

Another disadvantage of the vertical section is that it affords little opportunity to detect faulty equilibrium. Thus, as in the present paper, if an isotherm is constructed at 244.7°C . (the ternary eutectic temperature), it will become apparent that the extension of the corresponding eutectic line to low antimony concentrations, as in Fig. 8,* is of doubtful validity; here the line should probably end at about 4 per cent of antimony on the boundary of a field of $\text{Pb} + \epsilon$. The fact that thermal arrests were found at lower antimony concentrations should not be supposed to mean that a transformation may occur in that range, but rather that equilibrium was not attained; coring effects can easily give rise to false thermal indications of this kind. Other inconsistencies can be detected in the same diagram. For example, if it is assumed that the liquidus points are correct and an isotherm is con-

structed accordingly at 280°C ., it will be seen that the boundary between the liquid + ϵ and liquid + $\text{Pb} + \epsilon$ fields is slightly (0.5 per cent) too far to the right; this is the most probable direction of error if the disturbing effects of coring are present.

In the interpretation of vertical sections still more troublesome deficiencies appear. Returning to Fig. 8 as an example, it will be observed that the epsilon phase is mentioned in a number of fields, but that there is no indication whatever of its composition. The same is true of every phase represented, except within the region of liquid alone. Even the use of a multitude of sections would not satisfactorily eliminate this objection, for they could not in themselves designate the concentrations of the pairs and trios of phases in equilibrium. Thus half of the potential value of the phase diagram is lost in the vertical section; it is possible to read transformation temperatures, but not the compositions of the phases involved. Isotherms, if used in sufficient numbers, give both kinds of information.

No disparagement of the present paper is intended in this discussion; indeed I am impressed by the evident excellence of the experimental techniques and the skill of the author in developing the diagrams of this complex system. It is my purpose simply to urge the use of isothermal instead of vertical sections.

B. BLUMENTHAL (author's reply).—It is, indeed, somewhat difficult to envisage that alpha crystals have little effect in initiating the precipitation of the beta phase, and vice versa. If, however, it is assumed that the eutectic crystallization is one in which individual solid solutions form simultaneously from a common melt, it is likely that the formation of these solid solutions retains its individual characteristics during the eutectic crystallization. Although there may be cases where crystals of one kind may act as nuclei for crystals of another kind, in the present case the crystallization of the constituents of the eutectic apparently proceeds independently.

The thermometer calibrations were made under the conditions of the experiments; i.e., separate calibrations were made for various rates of cooling with and without stirring. Because in the binary system the data con-

* Figs. 7 and 8 have been corrected since the Preprint was issued.

cerning the duration of the arrest at the eutectic temperature represent well-known information, they were not included in the tables. In the ternary system, they would not permit an estimate of the limits of solid solubility at the eutectic temperature, since only a small portion of the whole system was investigated and the data are not accurate enough when the eutectic crystallization is preceded by an uncompleted peritectic reaction. The stirrer was a Pyrex glass rod of 5-mm. diameter with propeller-like blades, which were rotating directly under the bulb of the thermometer. Microscopic observations confirmed the diagrams, and since they did not give additional information it was felt that the reproduction of photomicrographs was not really necessary.

The author wishes to express his thanks to Dr. Rhines for calling his attention to the obvious error of ending the eutectic line at too low an antimony content (Figs. 7 and 8). The necessary corrections have been made in these diagrams.

Regarding the limits of the liquid + ϵ and liquid + Pb + ϵ fields, the conclusion is jus-

tified that if the liquidus points are correct, the limit is about 0.5 per cent too far to the right. This makes the observed temperatures about 3°C. too high, whereas it may be expected that if coring is the cause of inaccuracy the beginning of the secondary eutectic crystallization would be found at too low a temperature. Since the discrepancy is slight, I preferred to present the data as they were actually observed.

I concur with Dr. Rhines that it is desirable to present isothermal as well as vertical sections. A similar discussion followed F. D. Weaver's paper on the constitution of the lead-antimony-tin alloys.¹¹ It may again be stated that the ternary diagram covered by the present research is only a small part of the whole and the limits of solid solubility, particularly of the lead phase, were not determined. Consequently, horizontal sections could be drawn only with certain approximations and estimation of solid solubilities for which a quantitative basis was not available. Therefore, it seemed preferable to bring the vertical sections as the direct presentation of the experimental results.

Constitution of the System Indium-zinc

By F. N. RHINES,* MEMBER A.I.M.E., AND A. H. GROBE†

(New York Meeting, February 1944)

THE constitution of the indium-zinc alloy series has been investigated by Wilson and Peretti,¹ who determined the liquidus and eutectic temperatures by the conven-

tion of its alloys desirable. As a part of a program for the reexamination of the constitution of indium alloys by precision methods, the indium-zinc phase diagram

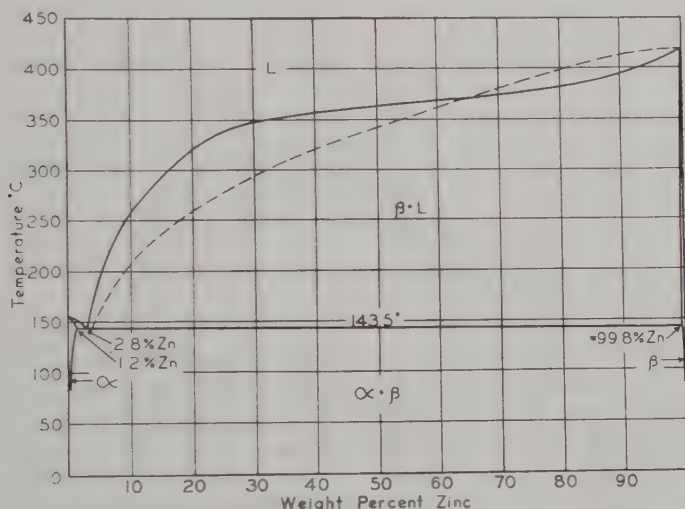


FIG. 1.—PHASE DIAGRAM OF INDIUM-ZINC SYSTEM.

Solid lines represent the new data; see Table 1 for experimental values. The dashed liquidus is taken from the work of Wilson and Peretti.¹

tional method of cooling curves and the eutectic composition by analyzing eutectic exudations. Recent developments affecting the availability of indium and consequent increased interest in its applications make a more complete knowledge of the constitu-

(Figs. 1 and 2) has been redetermined in its entirety. The eutectic temperature (143.5°C.) reported by Wilson and Peretti has been confirmed exactly, but their value of the zinc concentration at the eutectic, 4 per cent, was found to be high; the new value is 2.8 per cent of zinc.

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* Assistant Professor of Metallurgy and Member of the Staff of the Metals Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pennsylvania.

† Research Assistant, Metals Research Laboratory, Carnegie Institute of Technology.

¹ References are at the end of the paper.

tively indicated. By way of a general survey of the mechanical properties of these alloys, stress-strain curves in compression have been determined over the

samples remained in the form of residues from chemical analysis. These were reserved for the ultimate recovery of their indium content.

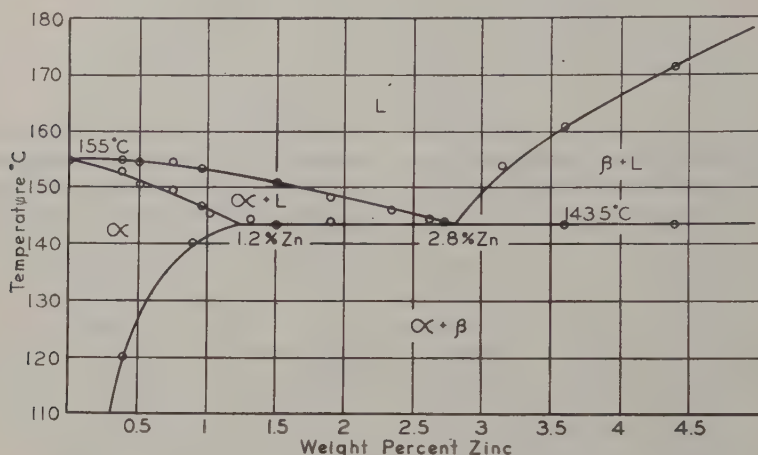


FIG. 2.—DETAIL OF INDIUM-RICH SIDE OF INDIUM-ZINC PHASE DIAGRAM.

entire range of compositions and a summary of these is included.

EXPERIMENTAL METHODS

Only $\frac{1}{4}$ lb. of electrolytic indium was available for this research. In order to make all of the desired measurements with this relatively small supply of metal, a program was established in which one alloy composition at a time was examined completely; the next alloy composition was then made by the addition of zinc. Beginning with a 60-gram sample of pure indium, 0.5 per cent additions of zinc were made until the eutectic was passed, after which the zinc concentration was advanced in larger steps. In all, 60 alloys were examined. Cooling curves, liquation tests and compression tests were made in succession upon the whole sample. A piece weighing approximately $1\frac{1}{2}$ grams was then set aside for chemical analysis, X-ray diffraction and metallographic studies; the remainder was used for the next alloy. By the end of the program, all of the indium except a small quantity retained for metallographic

METALS

The metals used in this research were the purest available in the year 1939. Typical electrolytic indium from the lot from which the indium was drawn contains 99.92 per cent In with the balance mainly Pb, Sn and traces of Sb, Zn, Cd, As, Ag, and Cu. Horsehead special zinc such as was used may be assumed to contain 99.994 per cent Zn with a maximum of 0.002 per cent each of Pb, Fe and Cd and traces of Sn and Cu. Both of these metals appear single phase upon metallographic examination (Fig. 3a).

Because of the repeated melting of the alloys, it was necessary to exercise special care in order to avoid progressive contamination. When molten, the metal was brought into contact with nothing except an alumina crucible, mineral oil or charcoal as a cover, a graphite mold and Pyrex glass thermocouple tubes (a few of the zinc-rich alloys were also heated to liquation in a salt bath). As far as possible, contact with the air was avoided. When solid, the alloys were handled in steel fixtures. No evidence of

contamination was found spectrographically or in the course of metallographic studies.

LIQUIDUS DETERMINATIONS

Low-melting alloys are especially subject to undercooling; reliable measurements of the liquidus temperatures are possible, therefore, only when measures are taken to allow nucleation to occur. A special furnace of a design proposed by C. S. Smith² was constructed for the thermal analyses. This furnace is so arranged that heat is withdrawn from the sample at any desired constant rate. In order to maintain the cooling rates to low temperatures it was found necessary to add an external water cooling coil to the equipment described by Smith. The specimen holder was a crucible ($1\frac{1}{2}$ in. outside diameter, $\frac{3}{4}$ in. inside diameter and 2 in. deep) cut from Armstrong "Non-Pareil" brick and lined with high-purity alumina cement. Two thermocouples were used: one, a differential Chromel-Alumel thermocouple having one junction within the crucible and the other junction outside, was used to actuate the furnace controller; the other, a platinum-platinum rhodium thermocouple of very fine wire (No. 33), encased in a thin-walled Pyrex glass tube about $\frac{1}{8}$ wide in diameter, was connected to a type K potentiometer for temperature measurements.

In the absence of transformations the time-temperature curves are nearly linear. By selecting a slow cooling rate, undercooling is minimized but not entirely eliminated. A short extrapolation of nearly straight segments of the cooling curves to their mutual intersection gives a satisfactory estimate of the true liquidus point where undercooling has occurred. A cooling rate of about $\frac{1}{2}^{\circ}\text{C.}$ per minute was used in these studies. Both faster and slower rates were tried, but it was found that undercooling was too pronounced at faster rates and the advantage of slower rates was too small to justify the greater expenditure of

time. Duplicate cooling curves were made with a large proportion of the alloys studied.

Accurate temperature measurement was ensured by the use of a fine-wire thermocouple to prevent heat loss by conduction along the wires, by the use of a thin-walled protection tube well centered in the melt, by frequent calibration of the thermocouple and by the use of sensitive measuring equipment. The temperature readings could be reproduced within a variation of 0.1°C. The accuracy of temperature standards in this range is a little better than 0.5°C. It seems reasonable to assume, therefore, that the temperature readings are reliable to 0.5°C. or less. This degree of precision is more than sufficient, since it could not be matched in the chemical analyses, which are equally important in establishing the liquidus points. The data obtained are recorded in Table I.

The nearly horizontal course of the liquidus in the range 35 to 75 per cent Zn suggests the possibility that a region of two-liquid immiscibility might appear at higher temperatures. To test this possibility, molten samples were quickly cooled after being held for 24 hr. at temperatures up to 650°C. No separation into layers could be detected. Two cooling curves exhibited inflections at 500° and 530°C. , but these could not be reproduced and accordingly were judged to be spurious.

SOLIDUS DETERMINATIONS

Points on the solidus curve read from time-temperature cooling curves are generally unreliable because of the excessive times necessary to attain equilibrium. More trustworthy results are obtainable by observing the temperature at which the liquation of the homogeneous solid alloy begins. The liquid first appears at the grain boundaries and can be detected either by the metallographic examination of quenched specimens or by observing the rupture of a lightly loaded bar of the alloy

during slow heating. Although the metallographic technique is generally favored, the mechanical method is much less laborious and has been shown to be equally

TABLE I.—*Experimental Results*

Zinc, Weight Per Cent	Liquidus Temperature, Deg. C.	Solidus Temperature, Deg. C.	True Stress (σ) at 10 Per Cent Strain
0.38	155	152.8	
0.50	154.5	150.6	
0.75	154.5	149.5	
0.97	153.1	146.4	149
1.10		145.3	
1.23	152.3	144.4	
1.31			168.8
1.52	150.7	143.4	
1.89	148	144	
2.34	145.8		163.2
2.61	144.5		
2.73	143.8		
3.15	153.7		
3.48			266.4
3.61	160.6	143.5	
4.39	182	143	200.8
5.42	196	143.5	176.8
6.53	224.3	143.5	172.2
7.58	239.5	143.5	
8.61	253.5	143.5	142.8
10.70	262.8		154.8
12.57	276	143	153.2
14.68	288.8		147.6
16.68	300.7		141.6
18.57	313.8	143	153.6
20.46	319.6		164
22.35	328	143.5	168.8
24.53	337.8		174.8
26.40	342.4		
28.50	343.1	143.5	
31.32 ^a	343.1	143	
32.17 ^a	345	143.4	
33.25 ^a	343.2	143.4	
35.70	352		
36.46 ^a	346		
38.03 ^a	348.9	143.4	
38.61 ^a	349.9		179.2
39.66	355		196.8
41.18	360	143.4	260
42.94	361	143.8	272.4
46.55	362.6		266
47.62 ^a	357.8		
51.91	363.5		280.8
54.48	365.6	143.4	321.4
55.98	367.8		356.8
57.92	369		419
60.70	370.1		605
64.46	369		
67.14	372.7	144	592
68.75	371		
74.50	375.8		918
82.37	379.3		932
86.93	381		
90	394.8		
95.08	405		
96.36	407		
98.3	415		
99	416		
99.2		369 ^b	
99.4		367 ^b	
99.6		369 ^b	
99.8		390.6 ^b	
99.9		398.3	2,300

^a Analysis in doubt; point not on the liquidus as plotted.

^b Not reproducible; not used in the construction of the phase diagram.

accurate provided that the structure of the metal is such as to permit rupture when the first trace of liquid appears and provided that no embrittling solid phase is present. Experience has shown that, if the bar breaks at the same temperature in a series of tests with varying heating rates, it is safe to assume that the rupture method is applicable; this was proved to be true with indium-rich alloys and the method was adopted.

The equipment was the same as that used for an earlier study of lead-antimony alloys and has been fully described elsewhere.³ A duplicate apparatus was constructed to permit the use of both an oil heating bath in the low-temperature range and a salt bath in the higher temperature range. The samples were made by remelting the alloys in the thermal analysis furnace, casting bars $\frac{3}{8}$ in. in diameter by about $\frac{3}{4}$ in. long in a graphite mold and forging these cold to a form that permitted cutting out bars $\frac{1}{8}$ by $\frac{1}{4}$ by 1 in. These were homogenized for periods of 1 to 3 days at 135°C. in an air furnace, from which they were transferred directly to the oil or salt bath. The temperature of the bath was increased as rapidly as possible to a point about 10° below that of the expected break, where it was held for a few minutes, and then increased at a rate of less than $\frac{1}{2}$ ° per minute until the bar had ruptured.

From 1.2 to 96 per cent of zinc the break always occurred at or very near the eutectic temperature 143.5°C. (Table I). At the low zinc concentrations a self-consistent series of solidus points was obtained. The intersection of these with the eutectic isotherm indicates a maximum solubility of 1.2 per cent of zinc in indium. At higher zinc concentrations the rupture occurred above the eutectic temperature, but the readings were not reproducible except near pure zinc. Evidently the small quantity of the eutectic alloy forming at high zinc concentrations was insufficient to cause rupture consistently at the eutectic temperature.

Apparently reliable points on the solidus were found only at compositions above 99.7 per cent of zinc. The limit of the solid solubility of indium in zinc at the eutectic temperature and the terminus of the solidus curve, therefore, has been estimated to be about 0.2 from the solid solubility data.

SOLID SOLUBILITY LIMITS

The intention was to determine the limits of solid solubility by the X-ray diffraction method using a high-temperature camera, but this proved to be impractical because the reflections were so diffuse that their measurement was impossible. Even when the alloys were quenched to room temperature from a homogenizing heat-treatment, satisfactory diffraction patterns could not be obtained. The X-ray patterns, however, gave clear evidence that no intermediate phases were present. This conclusion was supported by the microstructure of an indium-zinc couple, which, after being annealed for 60 days at $140^{\circ}\text{C}.$, exhibited no intermediate phase layer.

As an alternative the familiar metallographic technique was tried. Cast samples of the indium-rich and zinc-rich alloys were annealed for periods up to two weeks at $140^{\circ}\text{C}.$, were quenched and were aged at 130° and $120^{\circ}\text{C}.$ Another group of cast samples was annealed successively at $120^{\circ}\text{C}.$ and $140^{\circ}\text{C}.$, with metallographic examination after each treatment. It was found that the disappearance of the minor phase could be observed in both the high-zinc and low-zinc alloys, but that its reprecipitation could not be detected with certainty in either case. Actually, the precipitation of zinc particles in the indium-rich alloys was observed repeatedly, but it proved to be so difficult to distinguish with certainty between etch pits and precipitate particles that the evidence so obtained could not be used. From these observations, it was concluded that the solubility of zinc in indium falls rapidly with decreasing temperature to about 0.9 per cent Zn at

$140^{\circ}\text{C}.$ and 0.4 per cent zinc at $120^{\circ}\text{C}.$; the solubility of indium in zinc at $140^{\circ}\text{C}.$ seems to lie between 0.2 and 0.1 per cent In and at $120^{\circ}\text{C}.$ below 0.1 per cent In. In the light of this evidence it appears reasonable to assume that the limit of solid solubility at the eutectic temperature can hardly be more than 0.3 per cent of In and not less than 0.2 per cent; the solvus curve has accordingly been terminated at 0.2 per cent of In.

MICROSTRUCTURE

Indium is an extraordinarily soft metal, which consequently presents unusual difficulties in metallographic preparation. If indium-rich alloys are smoothed on the ordinary type of metallographic emery paper, particles of the abrasive become lodged in the metal and are exceedingly difficult to remove. Microtomy is a possible alternative, but the flow in a cut surface is so extreme that the microstructure is masked. In the present investigation a compromise procedure concluding with an etch sufficiently strong to remove flowed metal was adopted. Indium-rich alloys were smoothed by cutting with a razor blade; this was followed successively by polishing with 600 carborundum on duck cloth, Gamal alumina in green soap on Selvyt cloth, finally etching with a mixture of approximately equal parts of a solution of 10 per cent CrO_3 in water and a solution composed of 6 grams of $\text{K}_2\text{Cr}_2\text{O}_7$, plus 20 c.c. of H_2SO_4 plus 12 c.c. of saturated NaCl solution in 300 c.c. of water. Zinc-rich alloys were polished in the conventional manner and were etched with a 20 per cent solution of CrO_3 in water to which had been added one per cent of Na_2SO_4 .

The eutectic (Fig. 3*b*) appears to be composed of lamellar (or acicular) particles of zinc (dark) in a matrix of indium (light). In the unetched alloy the zinc also appears light; the etch heavily attacks the zinc, leaving dark cavities. Two indium-rich alloys in the as-cast and annealed condi-



FIG. 3.—INDIUM-ZINC ALLOYS. $\times 100$.

- a.* Pure indium, cast, etched.
- b.* 2.73 per cent Zn, as cast, etched.
- c.* 0.38 per cent Zn, as cast, etched.
- d.* 0.38 per cent Zn, annealed 1 week at 140°C ., quenched, etched.
- e.* 0.97 per cent Zn, as cast, etched.
- f.* 0.97 per cent Zn, annealed 1 week at 140°C ., quenched, etched.

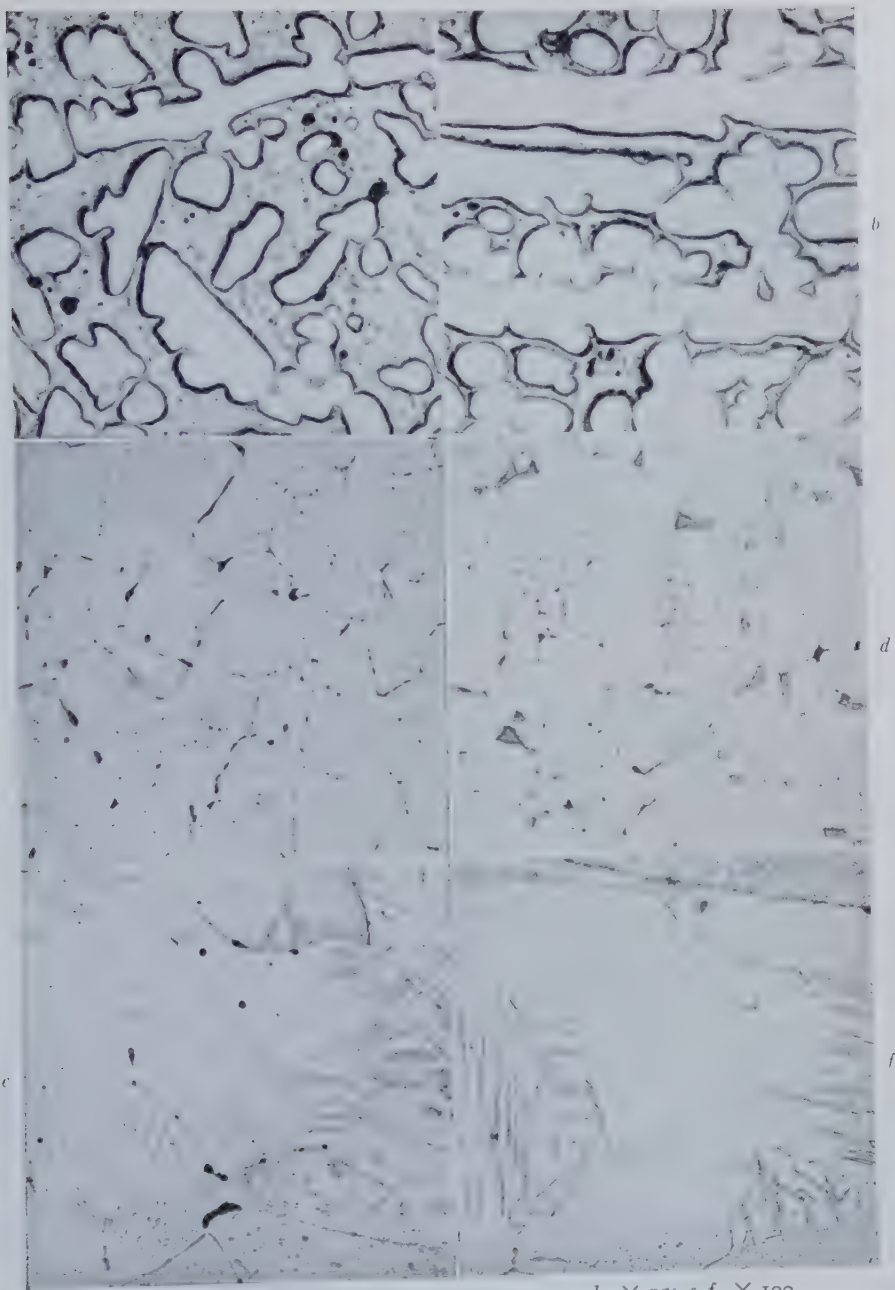


FIG. 4.—ZINC AS PRIMARY CONSTITUENT, *a* AND *b*, $\times 75$; *c-f*, $\times 100$.

- a*. 38.61 per cent Zn, as cast, unetched.
- b*. 74.50 per cent Zn, as cast, unetched.
- c*. 96.36 per cent Zn, as cast, unetched.
- d*. 96.36 per cent Zn, annealed 1 week at 140°C ., unetched.
- e*. 99.9 per cent Zn, as cast, etched.
- f*. 99.9 per cent Zn, annealed 2 weeks at 140°C ., etched.

tions are shown in Figs. 3*c*, *d*, *e* and *f*. The zinc phase is present in eutectic array in the as-cast alloy in both cases, but is completely dissolved when the lower zinc alloy

dezincing can occur is worth recording. It is noteworthy also that a rather large zinc loss upon repeated melting was found consistently.

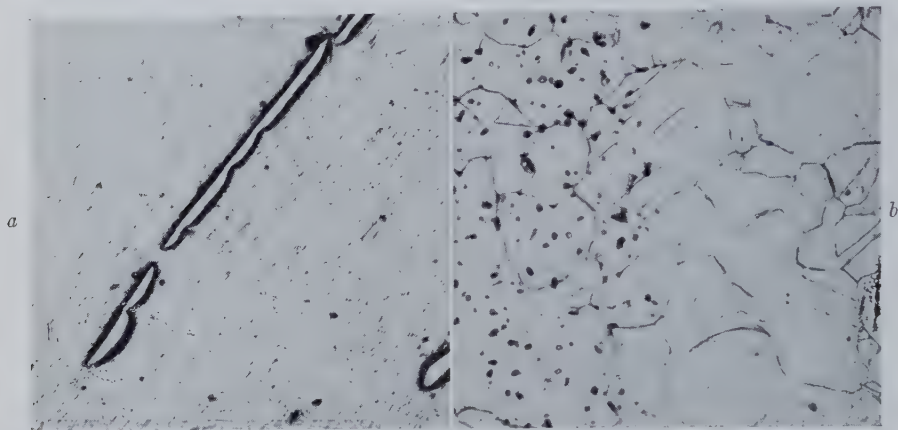


FIG. 5.—INDIUM-ZINC ALLOYS. $\times 100$.
a. 3.4 per cent Zn, as cast, unetched.
b. 2.49 per cent Zn, annealed, etched. Shows dezincing.

is annealed. It is noteworthy that all of the as-cast indium-rich alloys appear to have recrystallized, and that whenever plastic deformation has occurred, recrystallization follows at once. Evidently the recrystallization temperature lies below room temperature.

A group of alloys having the zinc present as a primary constituent is represented in Fig. 4. No etch has been used with the first four of these; the zinc phase appears as large light colored dendritic areas embedded in a matrix of the eutectic. Although the eutectic structure is not clearly delineated in the unetched surfaces, etched samples (not reproduced here) show that the zinc of the eutectic becomes segregated to the primary dendrites in high-zinc alloys; i.e., the eutectic is divorced. The dissolution of the indium phase upon heat-treatment is illustrated in Fig. 4*e* and *f*.

Evidence of dezincing was observed in one sample (Fig. 5*b*). Unfortunately, the history of this sample is not positively established; there is reason to suppose that it had been heated in contact with the air. In any event the observation that

CHEMICAL ANALYSES

Reliable methods for determining the composition of indium-zinc alloys in samples as small as those used in the investigation are not available. The usual procedures give highly erratic results. It was found necessary to develop new methods and these proved to be accurate only within limited concentration ranges. Alloys rich in indium were analyzed by a gravimetric method which has since been described.⁴ Those rich in zinc were handled by a potentiometric titration for indium, also described in the reference cited above. Some other techniques were used to a limited extent in the intermediate concentration ranges, but the values reported are chiefly those obtained by the first named methods.

Fortunately, a record of the "synthetic" composition of each alloy was available for the detection of large errors in analysis, and the regularity of the liquidus curves gave a further check. Near the two extremes of the concentration range, including the eutectic, it appears safe to assume

that the analyses are correct within a few hundredths of a per cent. Toward the middle of the range errors of at least one per cent could have eluded detection and

is to be had by the use of stress-strain diagrams made in compression tests. These are characteristically of the form shown in the example of Fig. 6. After

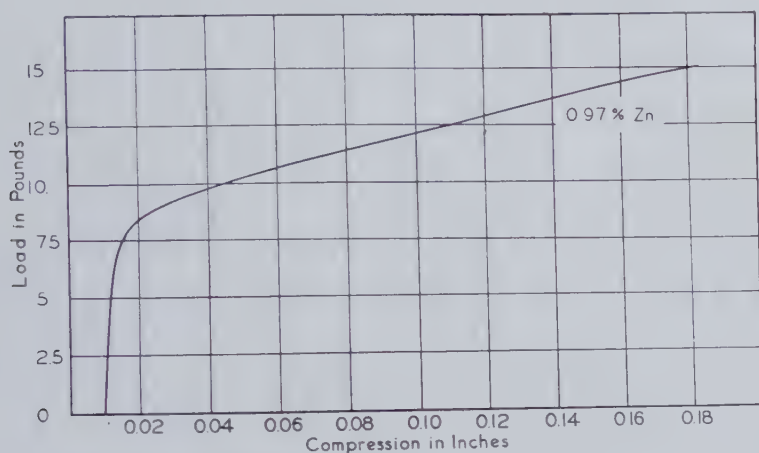


FIG. 6.—TYPICAL LOAD-COMPRESSION CURVE FOR ALLOY CONTAINING 0.97 PER CENT ZINC.

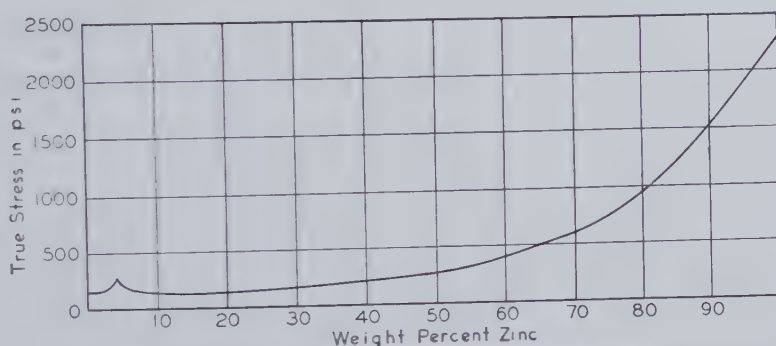


FIG. 7.—VARIATION OF TRUE STRESS σ , REQUIRED TO COMPRESS TO STRAIN OF 10 PER CENT, PLOTTED AS FUNCTION OF ZINC CONCENTRATION.

errors as large as 5 per cent were found. Where there was reason to suspect the validity of the analyses, the data were not used in plotting the phase diagram, but all points are recorded in Table 1.

MECHANICAL PROPERTIES

The usual measurements of tensile strength, elongation and hardness are of little significance in expressing the mechanical properties of extremely soft metals. A much better comparison of the properties in an alloy series of this kind

the initial rise, the curve tends to become straight. By choosing a definite deformation as a point of reference, expressed in percentage of initial length, the corresponding load values, corrected to true load (σ) for the individual alloys may be compared.

Samples for compression tests were made by casting cylinders $\frac{1}{4}$ in. in diameter by $1\frac{1}{4}$ in. long. These were brought to a standard form by compressing in a die $\frac{5}{16}$ in. in diameter. After sizing, the samples were annealed for a day at a

temperature of 135°C. The zinc-rich alloys were tested in a standard tensile testing machine; the indium-rich alloys responded to loads too low for the range of this machine and a special apparatus, using a calibrated steel ring for measuring the load, was built for testing in this range.

Values of σ at 10 per cent strain are plotted in Fig. 7 (see also Table I). Except for a sharp maximum at 3.48 per cent Zn, there is a steady rise in σ from pure indium to pure zinc. The intermediate maximum does not, as might be expected, occur exactly at the eutectic concentration. Its appearance at 3.48 per cent Zn might be supposed to be associated with a favorable particle size of the eutectic or of the primary zinc constituent, but the microstructure of the 3.48 per cent Zn alloy (Fig. 5a) gives little support to this view.

SUMMARY

The liquidus, solidus, and solvus curves of the indium-zinc phase diagram have been located. This is a simple eutectiferous system with the eutectic at 2.8 per cent Zn and 143.5°C. The limits of solid solubility lie at 1.2 per cent Zn in indium, and approximately 0.2 per cent In in zinc at the eutectic temperature, and diminish with falling temperature. Suitable metallographic techniques are described. In compression tests it is found that the true stress σ corresponding to a standard strain passes through a small maximum at 3.48 per cent Zn, but its value is exceeded in alloys containing 50 per cent and more of zinc.

ACKNOWLEDGMENTS

This investigation constitutes a part of the work supported at the Metals Research Laboratory of the Carnegie Institute of Technology through the generosity of the Bristol Myers Co. The indium was supplied through the courtesy of the American Smelting and Refining Co. Special thanks are due: to Dr. M.

Gensamer for designing the mechanical testing equipment and supervising its operation, to Dr. C. S. Barrett and Miss E. A. Saffer for the X-ray studies, to Mr. H. R. Hoge for his part in conducting the thermal analyses, to Messrs. C. W. Hopkins, R. J. Merdian and Miss W. Thompson for their work in making the chemical analyses, and to Mrs. W. M. Urquhart for developing the metallographic technique described in the paper.

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DISCUSSION

(John Ruzicka presiding)

E. A. ANDERSON,* Palmerton, Pa.—There is one point in this paper that I found rather interesting; the little peak on the compression curve. It happens in the actual table of data that the maximum stress is reported for an alloy of 3.48 per cent. Now we have noted in some single alloys very marked differentiations between the properties of the practically pure eutectic and the material on either side.

It might have been interesting had Dr. Rhines examined the compressive strength of the exact eutectic alloy to see whether the peak of such strength did coincide with the eutectic concentration. The value as now given might be interpreted to mean that the eutectic is a little higher than the value plotted on the curve.

F. N. RHINES (author's reply).—It is regrettable that we have no intermediate data that would properly answer that question. I can only say that the curve of Fig. 7 would have to turn upward very abruptly between 2.34 and 2.8 per cent Zn to place the maximum at the eutectic composition.

* Chief of Metal Section, Research Division, The New Jersey Zinc Company.

Liquidus Determinations in Zinc-rich Alloys (Zn-Fe; Zn-Cu; Zn-Mn)

BY GERALD EDMUNDS,* MEMBER A.I.M.E.

(New York Meeting, February 1944)

THE liquidus line on the phase diagram for temperature versus composition of a binary alloy system, representing the boundary between the homogeneous melt and the heterogeneous melt plus solid, besides showing the minimum casting temperature, is useful in determining eutectic compositions and the presence of phase changes such as peritectic transformations and intermetallic compound formation.

The liquidus often is determined by the cooling curves of thermal analysis, but supercooling frequently occurs, so that the temperature values are low. An alternative method, the one employed here, consists of determining the composition of samples of the melts from heterogeneous alloys that are at equilibrium. With meticulous attention to fundamentals, this method is capable of yielding values limited in precision only by the temperature control and measurement and analyses.

APPARATUS

By starting, on the one hand, with a supersaturated solution and allowing the excess solute to precipitate, and on the other hand with an undersaturated solution and allowing more of the solute to be dissolved, both processes being carried

out at the same temperature, equilibrium may be said to have been approached from both directions; that is, from *above* and from *below*. If the analyses show the solutions to contain the same fraction of solute when equilibrium has been approached from above and from below, one is assured that equilibrium has been reached in both determinations. In order to carry out such determinations, it is necessary to have equipment for obtaining and maintaining the proper temperatures; for holding the melt, measuring its temperature, and stirring, sampling and analyzing it.

The present work required temperatures from 420° to 900°C. The equipment consisted of:

A furnace, which was a vertical alundum tube, 1¾-in. diameter inside and 18 in. long, wound with Nichrome resistance wire, surrounded by a 3-in. i.d. alundum tube wound for 5 in. of length near each end, for compensation of end losses. This muffle was contained in an iron shell with Transite end plates, the intervening space being packed with Sil-O-Cel. The outside dimensions of the furnace were 12 in. in diameter by 18½ in. in height.

Heating current was supplied by three independent variable-voltage transformers (Variac), one connected to each end compensator winding and manually controlled, and one connected to the main winding through a series resistance of 5 ohms. This resistance was short-circuited for

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* Research Division, Technical Department, The New Jersey Zinc Company (of Pa.), Palmerton, Pennsylvania.

high current by a photoelectric potentiometric temperature controller operated by a thermocouple at the center of the furnace, between the inside and outside

to contain, stir and sample the alloys, and for melt thermocouple protection. The melts, sampling equipment, etc., were contained in open-top or sealed containers,

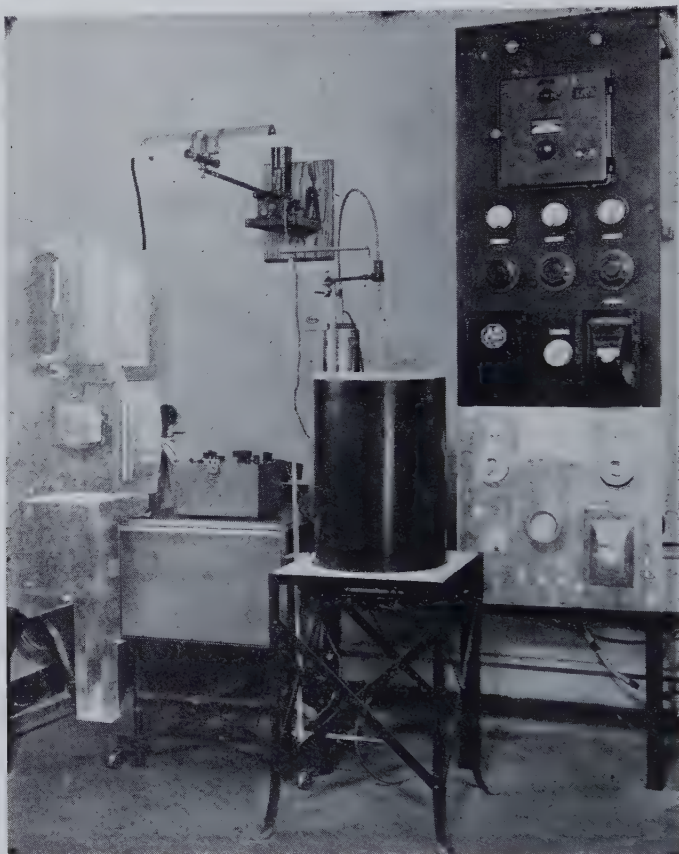


FIG. 1.—GENERAL ARRANGEMENT OF FURNACE AND CONTROL EQUIPMENT FOR LIQUIDUS DETERMINATIONS.

A type K Leeds and Northrup potentiometer and a more rigidly mounted thermocouple (Fig. 2) were used for measurement of melt temperature in all the tests reported here.

alundum tubes. A survey couple for determining the gradient along the length and inside of the furnace was mounted on brackets and a sliding support rod, so that it could be raised and lowered without appreciable disturbance of the furnace. The furnace and control equipment are shown by Fig. 1.

Pyrex glass, up to 610°C ., or silica for higher temperatures, both of which are resistant to zinc, was used for equipment

according as it was unnecessary or necessary to prevent either vaporization of the melt or its reaction with the atmosphere. The equipment for the various tests is illustrated by Fig. 3. The melt container rested upon a refractory plug (not shown), $1\frac{1}{2}$ -in. diameter by 6 in. long, in the bottom of the furnace tube.

A motor-driven apparatus, Fig. 4, mountable on top of the furnace, imparted about 140 cycles per minute of 180°

oscillatory rotation to a stirrer (Fig. 3-*H*), or the bulb for the sealed-tube method (Fig. 3-*I*), in which the sampling tubes, as baffles, agitated the melt.

OPEN-TUBE METHOD

The alloy is best prepared in the melt container used during sampling; for convenience, this may be done in another furnace.

The composition of the alloy must be gauged so that it will be partly molten, partly solid at the temperature of sampling, but there should not be enough solid to prevent clear samples of the melt. The proper composition may be determined by preliminary measurement or, frequently, by reference to previous determinations.

The alloy is then heated in the sampling furnace nearly to the sampling temperature, and the stirrer is mounted and started. The mechanical work of the stirring causes a slight increase in temperature. The agitation of the melt is continued for several hours, well beyond the time that seems necessary for solution, there being no way of determining when it should be discontinued unless samples are taken periodically—a troublesome and time-consuming procedure. When the stirring is stopped, the controller setting is adjusted manually to keep the melt at the maximum temperature attained during agitation; the motor drive assembly is removed, the melt is skimmed, the sampling tubes and breaker rods (suitably held in position in a cork, which also has a clearance for the thermocouple protection tube, supported by a clamp above the furnace) are introduced and the top opening of the furnace is closed with Transite plates and asbestos wool. The sampling-tube and breaker-rod group is not brought immediately to its final position but is first held for several minutes above the melt for preheating, and is then gradually lowered, over a period of several minutes, until the sampling tits are at the approxi-

mate vertical middle of the melt. During all of the time from discontinuance of stirring until several minutes after the sampling tubes have been brought to their



FIG. 2.—RIGIDLY MOUNTED CHROMEL-ALUMEL THERMOCOUPLE FOR MEASURING MELT TEMPERATURE.

The thermocouple wire passes from the hot junction (right) through the copper tube to the ice junction (left).

final position, the controller is adjusted manually to maintain a constant melt temperature. This is necessary because, notwithstanding all other precautions, the changes in heat loss from the top of the furnace and the change of melt depth

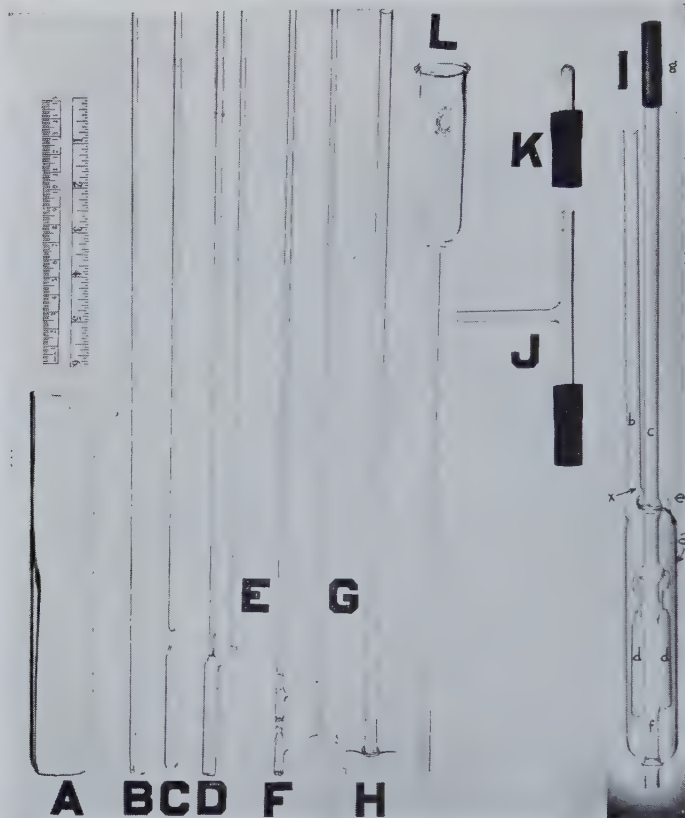


FIG. 3.—EQUIPMENT FOR CONTAINING, STIRRING AND SAMPLING MELTS. MADE OF PYREX GLASS OR SILICA.

- A. Open-top melt container.
- B. Spoon for skimming melt.
- C. Evacuated* sampling pipette (early type) for 10-gram sample.
- D. Evacuated* sampling pipette (later type) for 10-gram sample.
- E. Rod for breaking tit from sampling pipette.
- F. Evacuated* double sampling pipette for 3-gram samples.
- G. Rod for breaking tits from double sampling pipette.
- H. Stirrer and thermocouple protection tube for melt in open-top container.
- I. Bulb for sealed-tube method.
 - a. Melt container.
 - b. Filler tube, sealed off and removed at x after charging and evacuating container.
 - c. Central tube.
 - d. Sampling pipette.*
 - e. Vacuum release tit.
 - f. Drainage tube. The projection of this below the melt container rests in a hole in a Transite disk in the furnace for centering the lower end of the tube.
 - g. Friction-tape cushioning clamping in mechanical stirrer.
- J. Tee
- K. Stopper } used with bulb I.
- L. Funnel }

* The pipettes, while evacuated, are heated nearly to their softening temperature before the tits are sealed. Before use they may be checked for vacuum by glow discharge from a spark coil.

would otherwise slightly change the melt temperature. When stable temperature control is assured, the apparatus is left on automatic control, with occasional

temperature of the determination. Since the alloy has been produced without ever having been heated to a temperature above the determination, the melt cannot

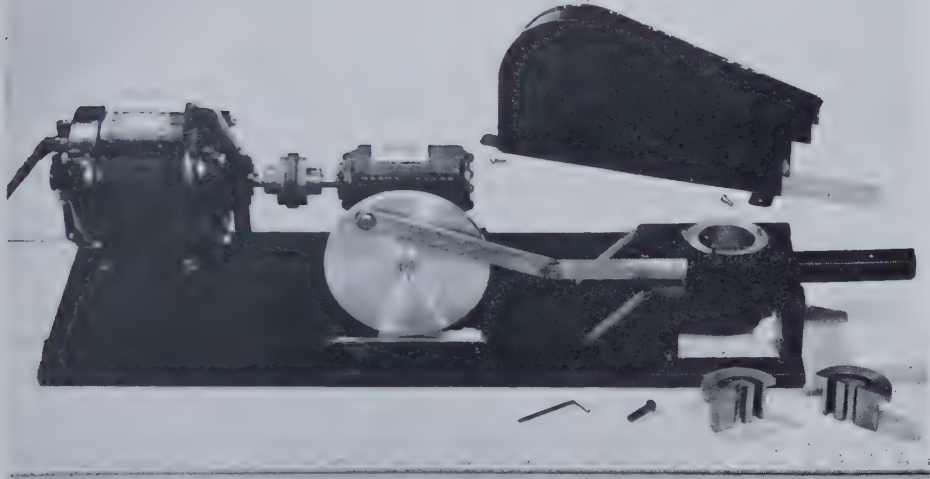


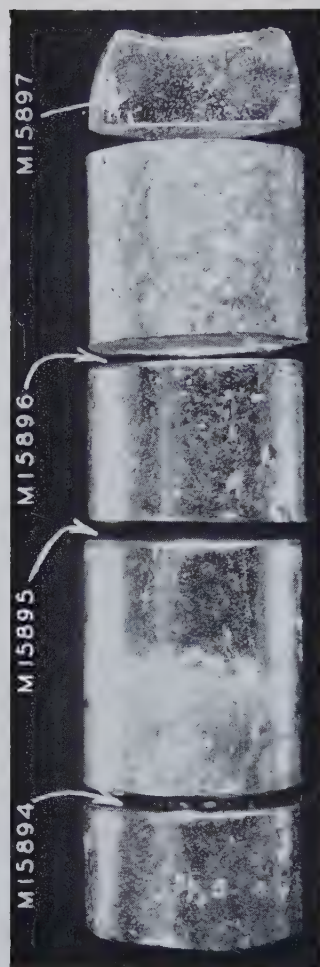
FIG. 4.—MOTOR-DRIVEN APPARATUS FOR OPERATING STIRRER, WITH GUARD AND STIRRER HOLDER REMOVED.

observations of temperature, to allow the solid constituent to settle or rise, according to its density relative to the melt. As with the stirring, the time required is unknown; therefore an excessive length of time is allowed. The tits are then broken from the sampling tubes by a slight, sharp tap directed downward on the top of the breaker rods, whereupon the sample is sucked into the evacuated tubes. After one minute has been allowed for complete filling of the tubes, they are removed from the furnace, cooled, cleaned of all adhering metal and skimmings, then broken for removal of the samples. The *entire sample* is used for analysis.

Summarizing, these samples are from a melt in equilibrium with a solid phase produced by diffusion of the molten solvent metal and the solid solute phase at the

contain more solute than the equilibrium liquidus composition, but may contain less if insufficient time of stirring has been allowed. Because of incomplete separation of melt and solid, the samples might contain some of the solute metal as solid particles drawn with the melt into the sampling tube; it is considered that if this occurred the amount involved would vary from sample to sample, so that the presence of an error would be obvious and the samples would be disregarded.

To obtain samples from a melt that has been supersaturated, the furnace temperature is next raised and the alloy stirred until all solute is in solution. This may be detected by feeling with a rod. (If the temperature required for solution exceeds that which is practical from oxidation, vaporization, or equip-

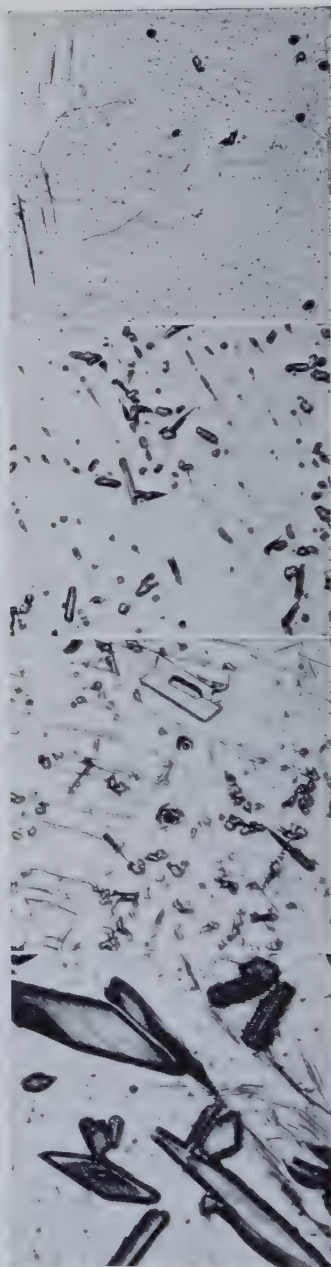


a

FIG. 5.—INGOT OF 0.1 PER CENT IRON-ZINC ALLOY AIR-COOLED FROM 475°C.

(Fe-Zn crystals form and settle rapidly, accounting for their scarcity in sample *b*. The samples from this alloy were taken from 4 in. and 2½ in. above the bottom of the melt container, at levels approximately equivalent to photomicrographs *b* and *c*, and analyzed 0.055 and 0.054 per cent Fe, respectively.)

a is about natural size. Photomicrographs *b-e*, $\times 24$.
Etchant: 20 grams CrO_3 , 1.5 grams Na_2SO_4 , 100 c.c. H_2O .



b (M15894). No large Fe-Zn crystals found in entire section

c (M15895). Largest Fe-Zn crystals found in entire section

d (M15896). Largest Fe-Zn crystal present in entire section

e (M15897). Many large Fe-Zn crystals present

ment considerations, samples are taken, using the regular sampling-tube breaker-rod assembly but without particularly close temperature control, and analyzed

of the solid phase; then samples are taken and analyzed, as before. To ascertain whether the proportion of solute is satisfactory for good melt sampling, the melt

TABLE 1.—*Experimental Data of the Zinc-rich Zinc-iron Liquidus Determination*

Equilibrium Approached from	Observed Temperature Deg. C.		Weight Per Cent Fe		Data Plotted in Fig. 6			
	Minimum ^a	Maximum ^b	Analysis	Admitted Variation in Analysis	1000 Abs. Temp. ^c		Atomic Per Cent Fe	
					Minimum	Maximum	Minimum	Maximum
Supersaturation ^d	423.5	425.6	0.014	± 0.001	1.436 ₆	1.430 ₂	0.015 ₂	0.017 ₆
	423.1	424.2	0.014	± 0.001	1.437 ₄	1.433 ₁	0.015 ₂	0.017 ₆
	422.6	424.1	0.014	± 0.001	1.438 ₄	1.433 ₁	0.015 ₂	0.017 ₆
Undersaturation.....	428.4	429.5	0.016	± 0.001	1.426 ₄	1.422 ₃	0.016 ₆	0.018 ₉
	428.4	429.5	0.015	± 0.001	1.426 ₅	1.422 ₃	0.016 ₆	0.018 ₉
Supersaturation ^d	473.7	475.4	0.055	± 0.001	1.339 ₉	1.335 ₁	0.063 ₂	0.065 ₆
	473.7	475.0	0.055	± 0.001	1.339 ₉	1.335 ₈	0.063 ₂	0.065 ₆
Undersaturation.....	474.7	475.9	0.055	± 0.001	1.338 ₂	1.334 ₂	0.063 ₂	0.065 ₆
Undersaturation.....	502.4	503.4	0.115	± 0.004	1.290 ₃	1.287 ₀	0.130 ₂	0.139 ₆
	502.4	503.4	0.111	± 0.004	1.290 ₃	1.287 ₀	0.125 ₂	0.135 ₆
	503.2	503.9	0.112	± 0.004	1.289 ₀	1.286 ₂	0.126 ₂	0.136 ₆
	503.2	503.9	0.113	± 0.004	1.289 ₀	1.286 ₂	0.128 ₂	0.137 ₆
Superaturation ^e	503.4	504.3	0.124	± 0.004	1.288 ₀	1.285 ₅	0.140 ₂	0.150 ₆
Supersaturation ^f	507.6	508.4	0.130	± 0.004	1.287 ₇	1.278 ₈	0.147 ₂	0.157 ₆
Undersaturation.....	521.9	524.4	0.174	± 0.004	1.258 ₇	1.253 ₁	0.199 ₂	0.208 ₆
	521.9	524.4	0.188	± 0.004	1.258 ₇	1.253 ₁	0.215 ₂	0.225 ₆
Supersaturation.....	523.5	525.0	0.192	± 0.004	1.256 ₁	1.252 ₂	0.220 ₂	0.229 ₆
	523.5	525.0	0.199	± 0.004	1.256 ₁	1.252 ₂	0.228 ₂	0.238 ₆
Undersaturation.....	526.2	528.9	0.185	± 0.004	1.251 ₉	1.246 ₂	0.212 ₂	0.221 ₆
	526.2	528.9	0.185	± 0.004	1.251 ₉	1.246 ₂	0.212 ₂	0.221 ₆
Supersaturation ^g	592.9	594.4	0.858	± 0.01	1.155 ₄	1.152 ₁	0.90 ₁	1.01 ₉
	592.9	594.4	0.800	± 0.01	1.155 ₄	1.152 ₁	0.93 ₁	0.958 ₉
Supersaturation ^h	606.3	607.0	0.901	± 0.01	1.137 ₈	1.135 ₆	1.04 ₂	1.06 ₅
	606.3	607.0	0.917	± 0.01	1.137 ₈	1.135 ₆	1.06 ₉	1.08 ₅
Undersaturation.....	607.4	608.2	0.827	± 0.01	1.135 ₁	1.134 ₀	0.95 ₅	0.97 ₉
	607.4	608.2	0.83 ₀	± 0.01	1.135 ₁	1.134 ₀	0.95 ₉	0.98 ₂

^a The lowest temperature observed during the last 24 hr. before sampling when equilibrium was approached from undersaturation, or, the lowest temperature ever observed when equilibrium was approached from supersaturation.

^b The highest temperature observed during the last 24 hr. before sampling when equilibrium was approached from supersaturation, or, the highest temperature ever observed when equilibrium was approached from undersaturation.

^c Less 0.5°C. for minimum; plus 0.5°C. for maximum.

^d Sample taken at about 511°C. analyzed 0.10 per cent Fe.

^e Sample taken at about 557°C. analyzed 0.26 per cent Fe.

^f Sample taken at about 549°C. analyzed 0.20 per cent Fe.

^g Values do not overlap; plotted with dashed lines.

^h Samples taken at about 614°C. Analyzed 1.11 and 1.06 per cent Fe.

ⁱ Sample taken at about 614°C. analyzed 0.913 per cent Fe. The ingot of the air-cooled melt contained a relatively small amount of iron-rich constituent. In view of these uncertainties, the graph has been drawn without inclusion of this value because it would require a considerable change in slope of the line, although the line could be so drawn and be consistent with all of the data.

for assurance that the melt contains more solute than is found by analysis when the alloy is cooled to the final sampling temperature.) The furnace temperature is then reduced to a few degrees above the sampling temperature and the sampling-tube, breaker-rod group is introduced as before. The temperature is then slowly reduced to the sampling temperature and automatically controlled there for a period sufficient to allow complete separation

container may be removed and air-cooled and the ingot examined. Microsections of the ingot will reveal at one end of it (according to the relative density of the melt and solid phase) a layer of coarse crystals of the phase that was solid at the test temperature (for example, Fig. 5), while the rest of the ingot will contain the solidified melt together with finer particles of second phase that have separated during air cooling.

SEALED-TUBE METHOD

For melts subject to rapid evaporation or reaction with the atmosphere, equilib-

beforehand. The required amount of solute in small pieces is introduced through the filler tube, the tee *J* with stopper *K* is attached, the bulb is evacuated, then

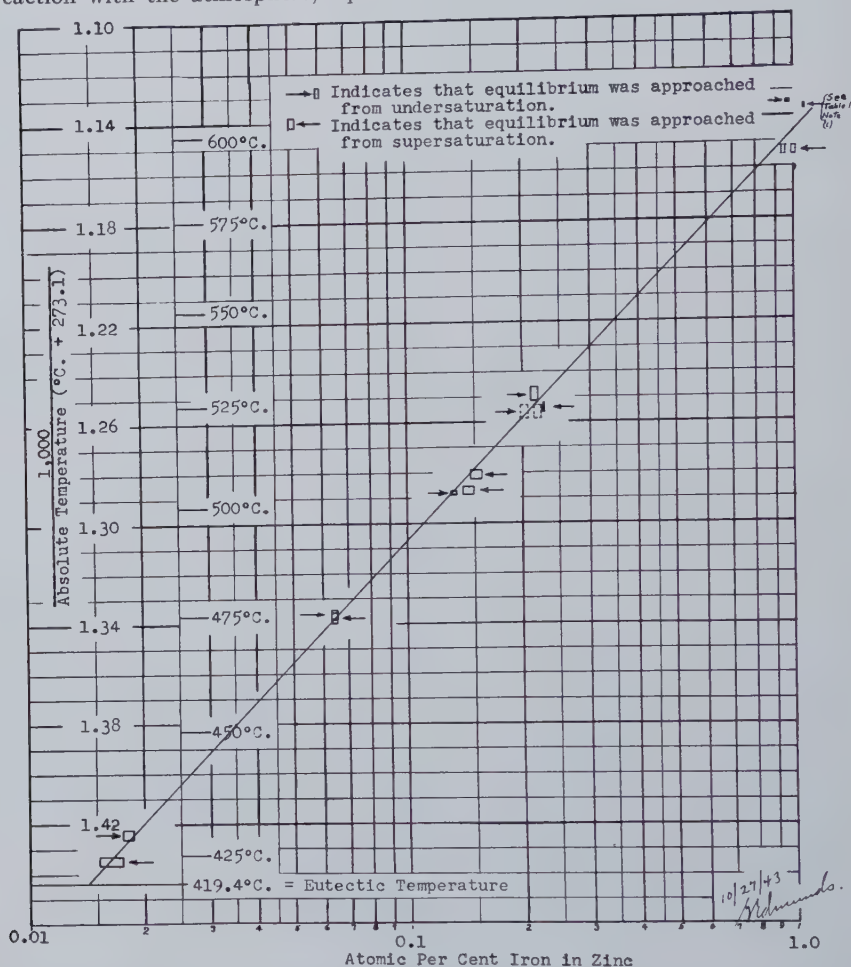


FIG. 6.—LIQUIDUS OF ZINC-RICH ZINC-IRON ALLOYS.

Plotted as logarithm of atomic per cent of iron versus reciprocal of absolute temperature.

rium is obtained by working with the alloy in a sealed container of the type shown in Fig. 3-*I*. The principles involved in this technique are basically the same as in the open-tube method, but the manipulation requires extreme care because of the fragility of the equipment. The alloy is made in the bulb, the volume of which must have been determined

lowered into the hot furnace. By continuing the evacuation, permissible only if the solute will not evaporate at the furnace temperature, adsorbed and occluded gases held by the bulb and solute are removed. The bulb is then filled through the tee with a gas inert to the alloy, stopper *K* is removed, funnel *L* is put in the filler tube and preheated with a gas flame,

molten zinc is poured in to within about $\frac{1}{2}$ in. of the top of the bulb, the funnel is removed, stopper replaced and the bulb

TABLE 2.—*Liquidus Values for Zinc-rich Zinc-iron Alloys*

Temperature, Deg. C.	Weight Per Cent Iron in Melt	
	According to Truesdale, Wilcox and Rodda ¹	According to Present Investigation
419.4 (Eutectic)...	0.018 ^a	0.012 ^a
425.....	0.02	0.014 ²
450.....	0.03	0.029 ^b
475.....	0.06	0.056
500.....	0.10	0.10
525.....	0.20	0.19 ^{3b}
550.....	0.30	0.31 ⁶
575.....	0.45	0.53 ^b
600.....	0.70	0.86
672 (Peritectic)....	3.0	3.02 ^a

^a Extrapolated.

^b Interpolated.

purpose; the bulb is then lowered, the stirring apparatus mounted and the attachment made with the central tube (*c* of Fig. 3-I). The melt thermocouple is inserted and supported so that its junction is about $\frac{3}{16}$ in. above the bottom of the central tube. The alloy is brought to temperature, stirred, and allowed to separate into its two phases by the same general procedures as have been described for the open-tube method. For sampling, the following operations are done in quick succession: the melt thermocouple is removed and slowly replaced by a flat-end breaker rod or tube, tit *e*, Fig. 3-I, is broken to admit air to the bulb and bring it to atmospheric pressure; the breaker rod is shoved sharply downward about an inch, breaking the bottom from the central

TABLE 3.—*Experimental Data of the Zinc-rich Zinc-copper Liquidus Determination*

Equilibrium Approached from	Observed Temperature, Deg. C.		Weight Per Cent Cu		Data Plotted in Fig. 7			
	Minimum ^a	Maximum ^b	Analysis	Admitted Variation in Analysis	1000 Abs. Temp. ^c		Atomic Per Cent Cu	
					Minimum	Maximum	Minimum	Maximum
Supersaturation.....	427.2	431.3	1.77	±0.05	1.429 ₀	1.418 ₆	1.77	1.87
	427.2	431.3	1.72	±0.05	1.429 ₀	1.418 ₆	1.72	1.82
	427.2	431.3	1.82	±0.05	1.429 ₀	1.418 ₆	1.82	1.92
Undersaturation.....	439.5	441.1	1.99	±0.05	1.404 ₃	1.399 ₆	1.99	2.10
	439.5	441.1	2.04	±0.05	1.404 ₃	1.399 ₂	2.05	2.15
	439.5	441.1	2.08	±0.05	1.404 ₃	1.399 ₂	2.09	2.19
Supersaturation ^d	529.8	530.2	5.68	±0.05	1.246 ₃	1.244 ₁	5.78	5.88
	529.8	530.2	5.70	±0.05	1.246 ₃	1.244 ₁	5.80	5.90
	529.8	530.2	5.73	±0.05	1.246 ₃	1.244 ₁	5.83	5.93
	529.8	530.2	5.74	±0.05	1.246 ₃	1.244 ₁	5.84	5.94
	528.3	530.1	5.66	±0.05	1.248 ₆	1.244 ₂	5.76	5.86
	528.3	530.1	5.67	±0.05	1.248 ₆	1.244 ₂	5.77	5.87
	528.3	530.1	5.67	±0.05	1.248 ₆	1.244 ₂	5.77	5.87
	528.3	530.1	5.66	±0.05	1.248 ₆	1.244 ₂	5.76	5.86
Supersaturation ^e	585.9	587.6	9.73	±0.05	1.164 ₈	1.161 ₂	9.93	10.03
	585.9	587.6	9.70	±0.05	1.164 ₈	1.161 ₂	9.90	10.00
Undersaturation ^f	594.1	595.0	10.54	±0.05	1.153 ₈	1.151 ₂	10.76	10.86
	594.1	595.0	10.52	±0.05	1.153 ₈	1.151 ₃	10.74	10.84
	594.1	595.0	10.57	±0.05	1.153 ₈	1.151 ₃	10.79	10.89
	594.1	595.0	10.58	±0.05	1.153 ₈	1.151 ₃	10.80	10.90

^a Same as footnote *a*, Table 1.

^b Same as footnote *b*, Table 1.

^c Same as footnote *c*, Table 1.

^d Open-tube method with hydrogen atmosphere.

^e Sealed-tube method. The tube was not sealed immediately, but a methane atmosphere was maintained in it overnight, after which a sample of the melt was obtained through the filler tube and the tube was then sealed off. The sample analyzed 11.9 per cent Cu.

^f Sealed-tube method.

again evacuated. The filler tube is sealed off at *x*, Fig. 3-I, with a torch after the bulb has been raised enough for that

tube and the sampling-tube tits. The bulb is removed from the furnace and the breaker rod is first shoved down to break

the top of the drainage tube, then raised to allow the melt to run out. The bulb is then cooled and broken and the samples

sample. The absolute accuracy of these has not been established, but great care has been taken to ensure a high order of

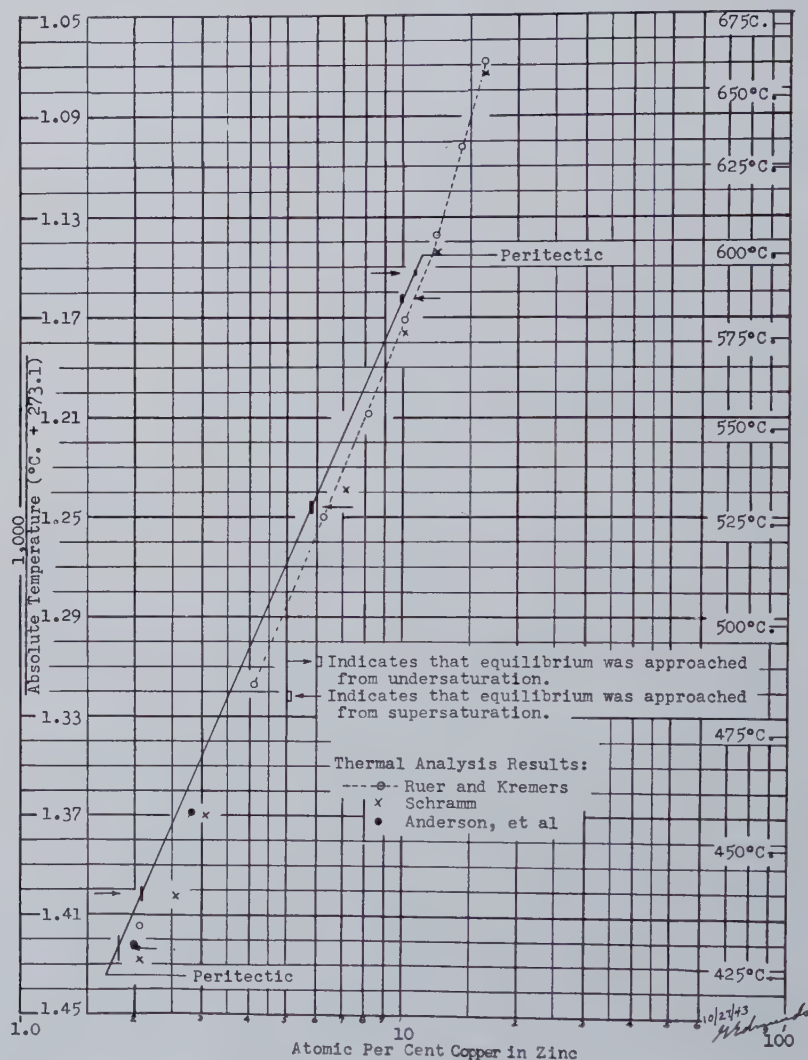


FIG. 7.—LIQUIDUS OF ZINC-RICH ZINC-COPPER ALLOYS.

Plotted as logarithm of atomic per cent of copper versus reciprocal of absolute temperature.

are removed and analyzed as in the open-tube method.

PRECISION OF MEASUREMENT

The data are the temperature of sampling and the analyzed composition of the

accuracy and recognized possible errors have been indicated on the plots by using boxes instead of points. Besides the estimated variation of analysis from true composition and an over-all allowance of $\pm 0.5^\circ\text{C.}$ for the several possible errors

involved in measuring temperature, the temperature dimension of these boxes takes into account the observed maximum departure over the last several hours from (1) the maximum temperature ever observed on a run approached from undersaturation or (2) the minimum temperature ever observed on a run approached from supersaturation. The observed maximum and minimum values may not represent the true range, since no continuous record of high sensitivity* was kept; however, usually the large variations occurred as a result of some attention to the experiment and observations could then be made. The fact that straight lines or smooth curves can be drawn to agree with all of the boxes for the plot of any liquidus branch is consistent with the allowances made.

LIQUIDUS OF SYSTEM ZINC-IRON FROM 422° TO 607°C.

The report on the liquidus of the zinc-iron system by Truesdale, Wilcox and Rodda¹ affords a basis for comparison of improved techniques. Also, the data of these authors depart somewhat from linearity,² particularly at the lowest temperatures and where the least departure would be expected, on a plot of the logarithm of atomic composition x versus the reciprocal of the absolute temperature T , and it was desired to test this relationship, since it could be useful in establishing eutectic compositions and in indicating other phase changes in alloys.

Alloys were made from a special lot of C.P. grade zinc† and intermediate alloys containing 0.1 or 4.1 per cent of Armco iron‡ alloyed with the same lot of C.P.

* A continuous Tapalog record was kept to spot any large variations; for example, one due to a temporary power interruption.

¹ References are at the end of the paper.

† Principal impurities, other than 0.0005 per cent Fe, are 0.0001 per cent Pb and 0.000027 per cent Cd.

‡ Typical analysis (see p. 3 of ref. 1): C, 0.012 per cent; Mn, 0.018; P, 0.004; S, 0.022; Cu, 0.044; Si, trace.

grade zinc. The open-tube method of liquidus determination with Pyrex glass equipment was used substantially as it is described above. The data obtained are given in Table 1 and Fig. 6. The results are all representable by a straight line on the $\ln x$ versus $1/T$ graph. A comparison of liquidus values from this and the Truesdale, Wilcox and Rodda investigation is given in Table 2. Considerable differences are noted near the eutectic (these values influence the determination, by extrapolation, of the eutectic composition) and at 600°C. By extrapolating to the 672°C. peritectic horizontal, the liquidus composition is 3.02 per cent Fe, agreeing with the value 3.0 per cent Fe reported by Truesdale and his co-workers. It may be significant that while this straight-line extrapolation of the $\ln x$ versus $1/T$ graph departs considerably from the liquidus values between 575° and 650°C. reported by Truesdale et al., the value at 672°C. agrees, and those investigators had used a different procedure for this and higher temperatures than for the lower temperatures.

LIQUIDUS OF SYSTEM ZINC-COPPER FROM 427° TO 594°C.

The liquidus for zinc-rich zinc-copper alloys has been determined from the cooling curves of thermal analysis by Ruer and Kremers,³ Schramm,⁴ and Anderson et al.⁵ The data obtained by these investigators for temperatures up to 600°C. have been converted to appropriate units and plotted as the $\ln_{10} x$ versus $1000/T$ in Fig. 7.

A few determinations have been made by the procedures described in this report. The zinc was from the same special lot of C.P. grade used for the iron alloys, and the copper was electrolytic. The results are given in Table 3 and are included on Fig. 7.

The new data fall upon a straight line on the $\ln x$ versus $1/T$ plot and this line

lies slightly above the lines drawn to represent the published data obtained by the cooling-curve method. The difference is small and in the direction expected; that is, the values reported from cooling curves are probably slightly low because of supercooling.

Zn-Fe alloys. The results are given in Table 4 and Fig. 8.

Before enough data were obtained to establish this liquidus curve, the investigation was discontinued. The results that were obtained do not lie upon a straight line on the $\ln x$ versus $1/T$ plot; they do

TABLE 4.—*Experimental Data on the Zinc-rich Zinc-manganese Liquidus Determination*

Equilibrium Approached from	Observed Temperature, Deg. C.		Weight Per Cent Mn		Data Plotted in Fig. 8			
	Minimum ^a	Maximum ^b	Analysis	Admitted Variation in Analysis	1000 Abs. Temp. ^c		Atomic Per Cent Mn	
					Minimum	Maximum	Minimum	Maximum
Undersaturation.....	440.5	443.0	1.70	±0.05	1.402	1.395	1.96	2.08
	440.5	443.0	1.69	±0.05	1.402 ³	1.395 ⁵	1.95	2.06
Supersaturation.....	444.0	448.2	1.81	±0.05	1.395 ³	1.385 ⁵	2.09	2.21
	444.0	448.2	1.82	±0.05	1.395 ⁵	1.385 ⁴	2.10	2.22
Supersaturation.....	484.8	485.5	3.42	±0.05	1.320 ⁵	1.317 ⁴	3.99	4.10
	484.8	485.5	0.60 ^d	x	x ³	x ³	^d	^d
Undersaturation.....	526.2	528.5	5.42	±0.05	1.251 ⁹	1.246 ⁷	6.33	6.44
	526.2	528.5	5.41	±0.05	1.251 ⁹	1.246 ⁷	6.32	6.43
Supersaturation.....	527.0	527.3 ^e	5.50	±0.05	1.250 ⁹	1.248 ⁷	6.42	6.54
	527.0	527.3 ^e	5.53	±0.05	1.250 ⁶	1.248 ⁶	6.46	6.57
Undersaturation.....	574.3	578.1	8.42	±0.05	1.180 ⁶	1.174 ¹	9.81	9.92
	574.3	578.1	8.45	±0.05	1.180 ⁸	1.174 ¹	9.84	9.96
Supersaturation.....	581.3	582.5 ^f	8.64	±0.05	1.171 ¹	1.168 ¹	10.0 ⁶	10.1 ⁷
Supersaturation.....	796. ^g	800. ^g	23.45 ^h	±0.05	0.936 ¹	0.931 ¹	26.7 ⁶	26.8 ⁷

^a Same as footnote a, Table 1.

^b Same as footnote b, Table 1.

^c Same as footnote c, Table 1.

^d Obviously incorrect; probably the tit accidentally broke from the sampling tube before the regular sampling.

^e Only three hours of settling.

^f Only eleven hours of settling.

^g No calibration was made of the thermocouple. The conversion was made from the standard Leeds and Northrup chart.

^h This alloy probably was contaminated slightly through accidental breakage of the thermocouple protection tube and consequent solution of part of the thermocouple.

Accepting the peritectic temperatures as 424° and 600°C., the respective liquidus compositions are 1.6₄ and 11.0 per cent Cu.

LIQUIDUS OF SYSTEM ZINC-MANGANESE FROM 440° TO 800°C.*

The manganese of Zn-Mn alloys reacts with the atmosphere, necessitating the use of the sealed-tube method for the liquidus determination. The alloys were made from electrolytic manganese, broken cathode sheet,⁶ and the same special lot of C.P. grade zinc that was used for the

lie along the smooth curve drawn to represent them in Fig. 8. It is entirely reasonable that the data fit a curve rather than a straight line, since the epsilon phase of the Zn-Mn system is a solid solution.* A discontinuity in slope in the curve would indicate a peritectic reaction, but a slight discontinuity would not be apparent unless many data were plotted.

Early published data on this liquidus curve were summarized by Hansen;⁷

* The furnace and control were not the same as were used for the Zn-Fe and Zn-Cu determinations.

* The equation $\ln x = -L/RT + C$ is derived with the assumption that L (the molal heat of solution) is constant, the solution is perfect, and the precipitating phase is a pure element or compound (not a solid solution of varying composition).²

subsequently it was redetermined by thermal analysis by Schramm,⁸ using 99.95 per cent Zn and 96.5 per cent pure

in Fig. 8. The thermal analysis data lie, as usual, below those determined by the equilibrium sampling method.

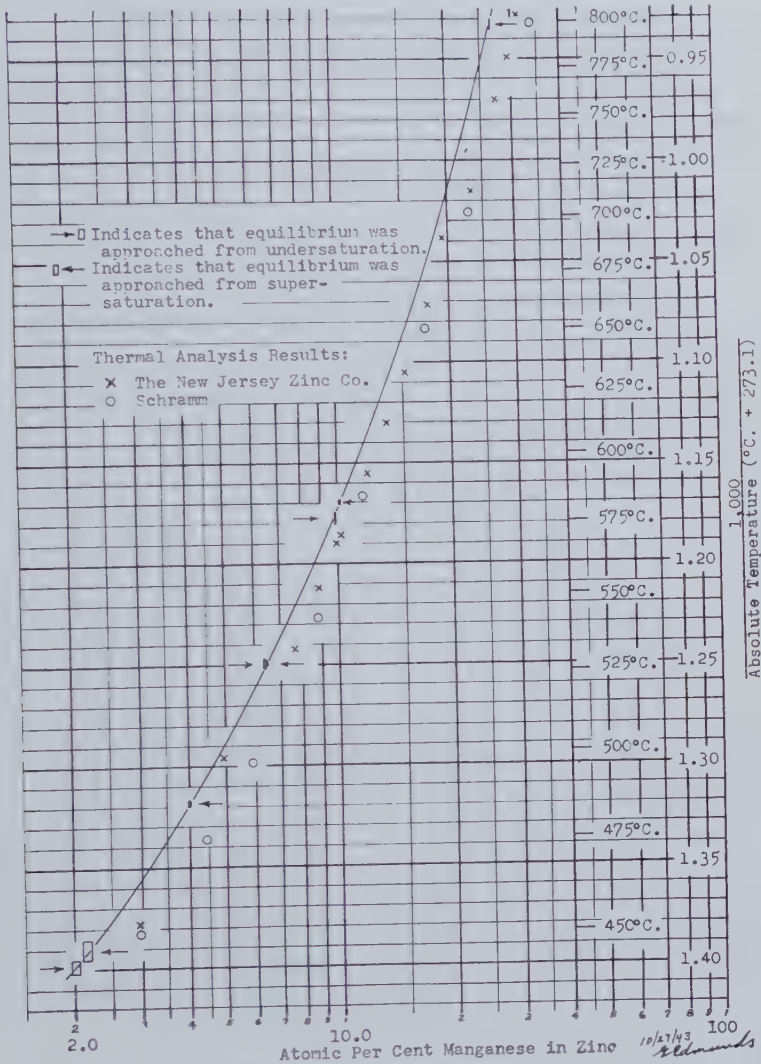


FIG. 8.—LIQUIDUS OF ZINC-RICH ZINC-MANGANESE ALLOYS.

Plotted as logarithm of atomic per cent of manganese versus reciprocal of absolute temperature

Mn, and by The New Jersey Zinc Co. (of Pa.) (unpublished data) using Special High Grade Zinc and electrolytic manganese. The results of the last and a few points from Schramm's curve are shown

SUMMARY

A technique for the accurate determination of liquidus points in zinc alloys has been described. This involves bringing a

partly molten, partly solid alloy to equilibrium and removing and analyzing a sample of the melt. By use of a special sealed container, alloys that are volatile or reactive with the atmosphere have been included for investigation.

Points on the liquidus curves have been determined for the systems:

Zn-Fe from 422° to 607°C.

Zn-Cu from 427° to 594°C.

Zn-Mn from 440° to 800°C.

In the Zn-Fe system, the eutectic composition is 0.012₂ weight per cent Fe.

In the Zn-Cu system, the liquidus compositions at the 424° and 600°C. peritectics are 1.6₄ and 11.0 per cent Cu.

ACKNOWLEDGMENT

The writer appreciates assistance given by several other members of the Research Division, Technical Department, The New Jersey Zinc Co. (of Pa.), and especially acknowledges the contributions of Dr. C. W. Siller and Messrs. J. R. Bossard and H. G. Bossard.

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DISCUSSION

(John Ruzicka presiding)

F. N. RHINES,* Pittsburgh, Pa.—I think that this paper is something of a classic, inasmuch as it represents a very ingenious adaptation of what was regarded as the classic method of determining liquidus curves 50 years ago to metals that heretofore have resisted the method. It is technically very sound, and I think that the approach is most interesting.

W. L. FINK,† New Kensington, Pa.—This method is really very useful. I think in general it gives more accurate results than can be obtained by cooling-curve methods, particularly when the slope of the liquidus curve is very steep.

We have used the method extensively in working on aluminum diagrams. We did not use quite the refinement of technique that was used here, and of course, we are unable to use glass or silica in contact with aluminum. It was necessary to use graphite crucibles and graphite stirring rods instead of the glass.

We did employ larger melts than were used by the author. That has the advantage of enabling one to take more samples without running out of material. We were able to take samples after two or three intervals at each temperature. If they all checked, we were confident that equilibrium had been attained. With this double check on equilibrium, the points all fall on the curve. That is an advantage.

There is an incidental use that can be made of the unused portion of sample that finally solidifies. By the time the experiment is completed, there will be some very large pieces of constituent at the bottom of the container, which (provided no peritectic was encountered) can be chemically separated and analyzed to determine the composition of the primary phase. It is advisable after the chemical separation to examine the pieces of constituent under the microscope and select enough well-formed, clean particles for the chemical analysis.

I would also like to call attention to the method of plotting the solubility curve (the

* Department of Metallurgy, Carnegie Institute of Technology.

† Aluminum Research Laboratories.

reciprocal of the absolute temperature against the logarithm of the concentration). It is very useful. It has been mentioned a number of times in the literature, but it has not been used as much as it should be. Generally speaking, the solubility curves are straight lines when they are plotted this way.

From the assumptions that are made in derivation of the equation one really would not expect straight lines as often as they are obtained. In our own work we suspect there is something wrong with the work if we do not get straight lines, and check the results thoroughly before we are willing to believe that the liquidus line is curved.

Sometimes a curved line indicates the presence of one or more peritectics. If the points are taken close enough together it is possible to show definitely that the liquidus is a series of straight lines, and that the intersections of those lines determine the peritectic temperatures very closely.

G. EDMUNDS (author's reply).—The methods of taking successive samples from a single melt, and of separating and analyzing the precipitate phase, both as discussed by Dr. Fink, have been employed on zinc alloys, but not for the particular cases reported in this paper.

Rolled Zinc-titanium Alloys

By E. A. ANDERSON,* MEMBER, E. J. BOYLE* AND P. W. RAMSEY,* JUNIOR MEMBERS A.I.M.E.

(New York Meeting, February 1944)

ONLY a few zinc-rich alloys are in commercial use today, and these depend largely upon solid solution effects for their desirable properties. Typical examples are rolled alloys containing about 1 per cent of copper, with or without additions of elements such as magnesium,¹ and die-casting alloys containing about 4 per cent of aluminum with small amounts of magnesium and sometimes copper.²

A number of elements are capable of forming alloys with zinc, which do not enter into solid solution except in limited degree. The present paper considers one such system, zinc-titanium, in which alloys having potentially useful properties in the rolled form were found.

ZINC-TITANIUM SYSTEM

The zinc-rich portion of the zinc-titanium diagram, as determined by standard methods in this laboratory,³ is shown in Fig. 1.

The portion of the diagram of significance in the present work extends from 0 to about 0.5 per cent titanium. Gebhardt⁴ places the eutectic at 0.45 per cent, but the evidence in favor of the composition given in Fig. 1 is considerable.

The solid solubility of titanium in zinc is very low indeed and possibly places these alloys in a somewhat different category from the commercial alloys previously mentioned.

Manuscript received at the office of the Institute Nov. 30, 1943. Issued as T.P. 1687 in METALS TECHNOLOGY, February 1944.

* Research Division, Technical Department, The New Jersey Zinc Co. (of Pa.), Palmerton, Pa.

¹ References are at the end of the paper.

ALLOY PREPARATION

All of the alloys used in this work were prepared with titanium metal of 98.9 per cent purity. In most cases high-purity zinc (99.99 per cent) was used but sufficient work was done later to show that zinc of about high-grade composition would yield approximately equal results. Best practice in alloy manufacture seemed to be to prepare a zinc-titanium hardener by adding about 4 per cent of titanium metal to molten zinc and holding under a boric acid cover, with frequent stirrings, at 750°C. until the titanium had dissolved. The desired titanium content could readily be obtained in the final alloy by adding the calculated amount of this hardener. The alloys proved to be quite stable in composition, unless overheated, and, with reasonable temperature control, required no cover or flux to prevent loss of titanium content by oxidation.

HOT-ROLLING TESTS

Three alloys containing, by analysis, 0.05, 0.12, and 0.23 per cent titanium were selected for preliminary study. Slab cross sections revealed a marked grain refinement* (Fig. 2) in the two alloys of highest titanium content. Cast unalloyed zinc has a columnar grain structure similar to that shown for the alloy of lowest titanium content but without the scatter of small equiaxed grains at the center.

* The presence and extent of this grain refinement was later found to be influenced by the presence of other elements, such as lead. No relationship between slab grain size and the properties of rolled strip was noted.

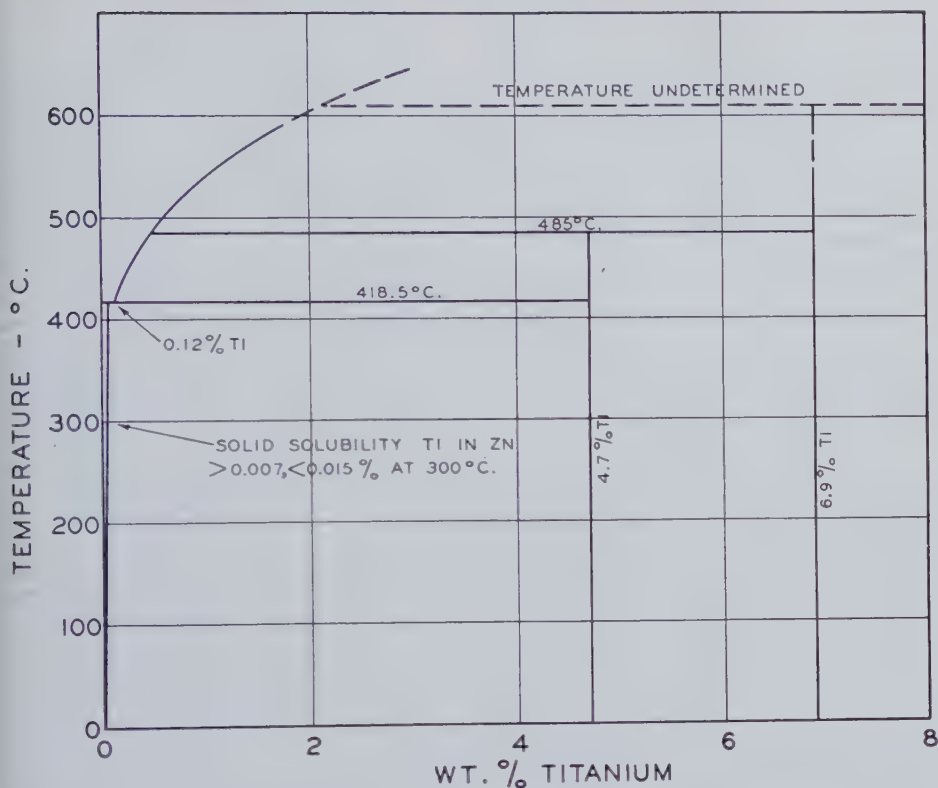
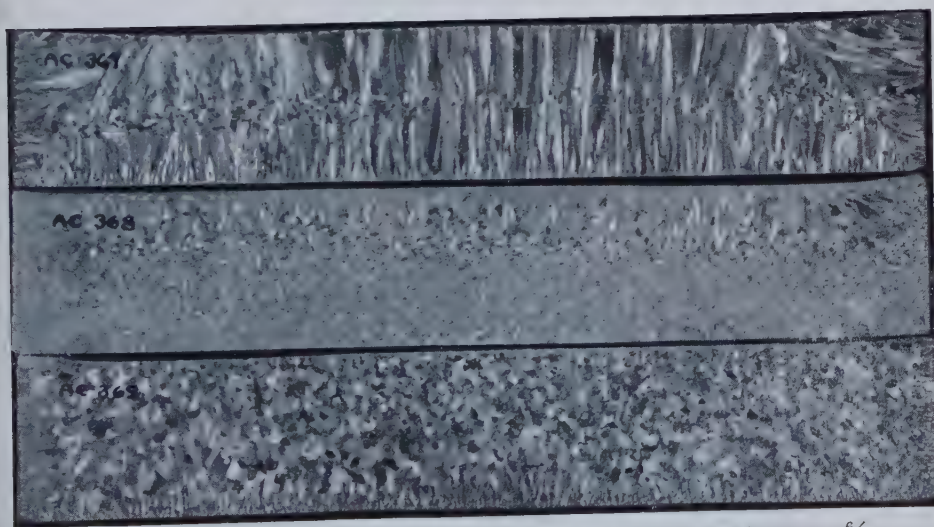


FIG. 1.—ZINC-RICH PORTION OF ZINC-TITANIUM DIAGRAM.

FIG. 2.—EFFECT OF TITANIUM ON GRAIN STRUCTURE OF CAST ZINC. $\times$ APPROX. 6%.
Top, 0.05 per cent Ti; middle, 0.12 per cent; bottom, 0.23 per cent.

These slabs were hot-rolled to 0.02 in. in a 12-in. diameter mill with a final coil temperature of about 200°C. The bars rolled easily and produced strip of good surface quality.

The rolled product was subjected to the normal routine tests for mechanical properties, including determinations of creep rate. Typical properties are listed in Table 1.* Included, for comparison, in this and many of the subsequent tables and figures are data for a typical solid solution type alloy, 99 per cent Zn, 1 per cent Cu.

The most interesting observations at this stage of the work lay in the creep data.† These are best seen in Fig. 3, where the inverse creep rates are plotted against stress on a log-log basis for a typical zinc-titanium alloy and the 1 per cent copper alloy. The difference in slope of the curves for the two alloys is striking. That this difference is inherent has been demonstrated by the fact that all of the many zinc-titanium alloys tested in this work as well as a series of zinc-iron alloys (a comparable system) gave test curves almost parallel to that shown here while several alloys of the solid solution type (zinc-cadmium, zinc-copper, zinc-manganese, etc.) gave test curves essentially parallel to that shown for the 1 per cent copper alloy.

* With-grain tensile tests were made on specimens whose length lay in the rolling direction. In the with-grain bend tests, the axis of the bend lay in the rolling direction. Across-grain tests were made on specimens 90° from the rolling direction in the plane of the strip. In all subsequent tables and figures, only the with-grain direction is considered.

† All creep tests in this work were made by dead weight loading, using the principles but not the apparatus discussed by J. Ruzicka.⁵ In most cases testing was at constant room temperature (25°C.). Creep rates are presented on an inverse scale as days per per cent elongation in order that the more creep-resistant materials may be represented by the larger values. In general, zinc materials in a reasonable stress range tend to produce straight lines when log stress is plotted against log inverse creep rate, but the relationship must not be taken for granted.

TABLE 1.—Composition, Mechanical Properties and Inverse Creep Rates for Hot-rolled Zinc-titanium Alloys and 1 Per Cent Copper Zinc

Alloy No.	Analyzed Percent- age Ti, Balance Zn ^a	Coil No.	Test Gauge, In.	Scler- oscope Hard- ness	Dynamic Ductility, In.	Temper, Per Cent	180° Bends ^b		Tensile Strength Lb. per Sq. In.		Tensile Elongation, Per Cent in 2 In.	Inverse Creep Rates, Days per Percentage Elongation, with Grain Stress		
							With Grain	Across Grain	With Grain	Across Grain	With Grain	8,000 Lb. per Sq. In.	12,000 Lb. per Sq. In.	15,000 Lb. per Sq. In.
AC367	0.05	E5426	0.023	19	0.320	36	X	X	19,500	27,600	33.2	24.8	0.055	0.0039
AC368	0.12	E5427	0.021	20	0.300	37	2½	2	20,100	29,900	29.5	190.4	1.05	0.023
AC369	0.23	E5428	0.022	22	0.295	40	3	2	21,300	30,000	28.3	1120.4	4.66	0.077
1% Cu		E5693 ^c	0.018	17	0.280	40	3½	2	23,700	30,000	35.0	1.95	0.16	No test

^a Alloys prepared with Horse Head Special zinc.

^b Values represent the diameter of the bend in multiples of sheet thickness. Small values indicate better bending properties.

^c Hot rolled, analogous to Zn-Ti treatment.

^d Tests not run to the usual 6 per cent total elongation. Values recorded represent the slope of the line joining the origin of the curve of time vs. elongation with the final recorded point. Values probably lower than true values.

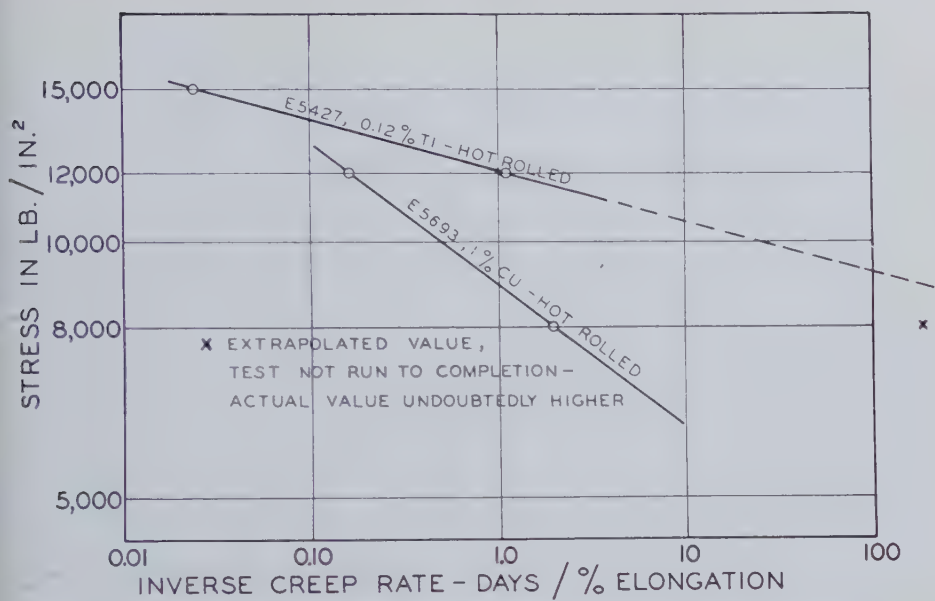


FIG. 3.—LOG STRESS VS. LOG INVERSE CREEP RATE FOR 0.12 PER CENT TITANIUM ZINC AND 1 PER CENT COPPER ZINC.

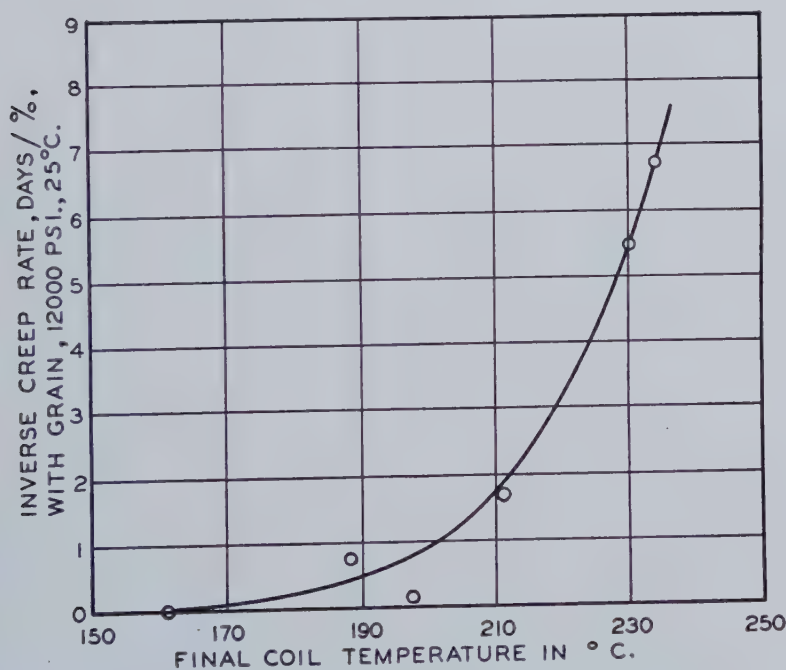


FIG. 4.—COIL TEMPERATURE VS. INVERSE CREEP RATE FOR ZINC-TITANIUM ALLOY.

The effect of the difference in slope is to place the zinc-titanium alloy in a position of increasingly superior creep resistance as the stress is decreased. The validity of extrapolations to very low stresses may be questioned, but the few data available indicate that the extrapolation is on the safe side for the zinc-titanium alloys.

EFFECT OF ROLLING TEMPERATURE

In the early stages of this work, it was observed that relatively wide variations in creep rate at a given stress seemed to correlate with the temperature of rolling. This correlation was verified in a series of tests on a single alloy (0.11 per cent Ti) which was rolled to final gauge with a range of final coil temperatures. The data are plotted in Fig. 4.

SELECTION OF ALLOYS FOR CONTINUED WORK

In order to permit a wider range of conditions of rolling, heat-treatment, testing, and so forth, to be considered, it was desirable to reduce the alloys under consideration to one composition. The choice was made of the alloy containing 0.10 to 0.15 per cent titanium with a nominal 0.12 per cent titanium. This, it will be recognized, is the composition of the eutectic and is the highest titanium content that will permit freedom from relatively coarse zinc-titanium compound particles. All experiments referred to in the remainder of the paper were carried out with this alloy.

EFFECT OF ROLLING CONDITIONS ON PROPERTIES

The hot-rolled alloy had properties of interest (Table 1). It fabricated well but fell slightly short of the commercial zinc alloys in drawing properties. It was found that a final 50 per cent cold-rolling would cause sufficiently better drawing properties to make the alloy of commercial

interest. As will be discussed later in the paper, the decrease in creep resistance brought about by this cold-rolling could be overcome by subsequent annealing. The effect of this rolling treatment on the properties may be seen in Table 2.

TABLE 2.—*Mechanical Properties of Zinc-titanium Alloy as Influenced by Rolling Treatment*

Alloy ^a	Rolled	Scler- oscope Hard- ness	Tensile Strength, Lb. per Sq. In.	Elong- ation, Per Cent	Inverse Creep Rate 8000 Lb. per Sq. In., Days per Per Cent
Zn-Ti	Hot	21	19,700	34	100
Zn-Ti	Cold	15	17,900	39	1.2
Zn-1 % Cu	Hot	17	23,700	35	1.9
Zn-1 % Cu	Cold	25	28,000	54	2.3

^a Zn-Ti alloy, 50 per cent cold final reduction; Zn-Cu alloy, 20 per cent.

The data in Table 2 reveal the unusual effect in the zinc-titanium alloy of cold-rolling effecting a softening and weakening as compared with hot-rolled material. The work-hardening revealed in the 1 per cent copper alloy is, of course, the normal experience. The softening effect in the zinc-titanium alloys is reproducible, as are the interesting microstructures shown in Figs. 5 and 6.

Photomicrographs of the hot and cold-rolled 1 per cent copper alloy (Figs. 7 and 8) show the former to be well recrystallized and the latter to be cold-worked. The zinc-titanium alloy, on the other hand, appears free of cold-working in the cold-rolled state, an observation that is consistent with the properties obtained.

Redraw tests showed that as many as four redraws could be made without intermediate anneals and with at least 95 per cent recovery. This again is consistent with the evidence that this type of alloy does not work-harden.

Basal-plane pole figures of the two alloys in the cold-rolled condition are shown in

Figs. 9 and 10. The 1 per cent copper alloy used in this case contained also 0.01 per cent magnesium.

The orientations shown in Fig. 10 are

properties has not been fully evaluated as yet, but no strong connection seems evident. The orientation effect also appeared in hot-rolled zinc-titanium alloys

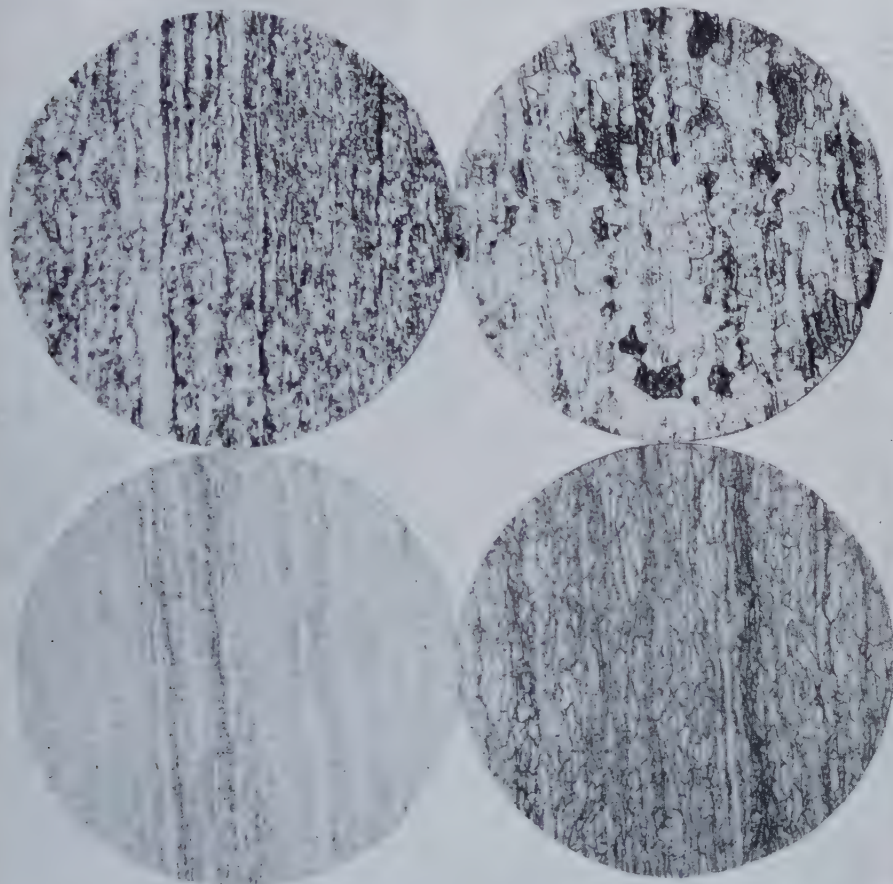


FIG. 5.—ZINC-TITANIUM ALLOY, HOT-ROLLED. $\times 200$.

FIG. 6.—ZINC-TITANIUM ALLOY, COLD-ROLLED. $\times 200$.

FIG. 7.—ZINC AND ONE PER CENT COPPER, HOT-ROLLED. $\times 200$.

FIG. 8.—ZINC AND ONE PER CENT COPPER, COLD-ROLLED. $\times 200$.

normal for zinc materials. The appearance of a high population of basal planes normal to the rolling plane and lying in the rolling direction (Fig. 9) is unusual and has never before been seen in this laboratory in zinc. The significance of this orientation texture in terms of directionality of

and was not removed for any rolling treatment by subsequent annealing.

EFFECTS OF ANNEALING

Contrary to experience with zinc, the zinc-titanium alloy has been found not to grow excessively large grains when

annealed (see Figs. 11 and 12). Anneals up to 24 hr. duration at temperatures up to 400°C . failed to produce grain

are not harmed by annealing and, most important, the high creep resistance noted in the hot-rolled alloy that was

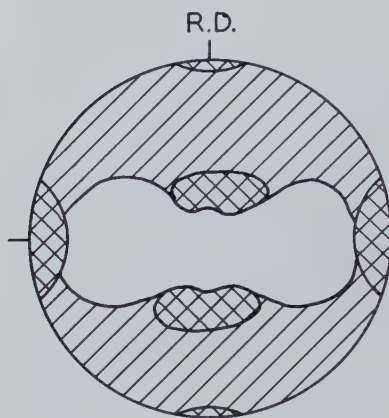


FIG. 9.

FIG. 9.—BASAL-PLANE POLE FIGURE FOR ZINC-0.12 PER CENT TITANIUM ALLOY COLD-ROLLED.
Plane of projection is rolling plane.

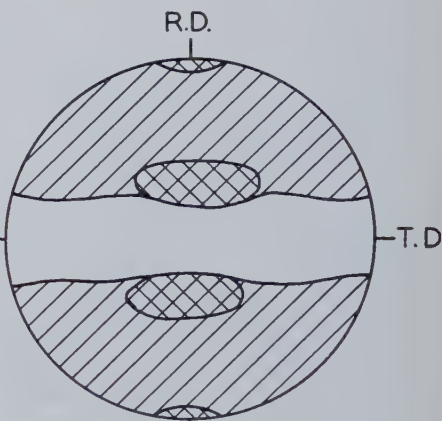


FIG. 10.

FIG. 10.—BASAL-PLANE POLE FIGURE FOR ONE PER CENT COPPER, 0.01 PER CENT MAGNESIUM ALLOY COLD-ROLLED.
Plane of projection is rolling plane.

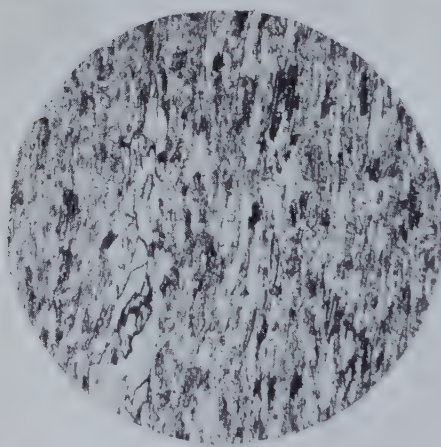


FIG. 11.

FIG. 11.—ZINC-TITANIUM ALLOY, 50 PER CENT COLD REDUCTION. $\times 200$.

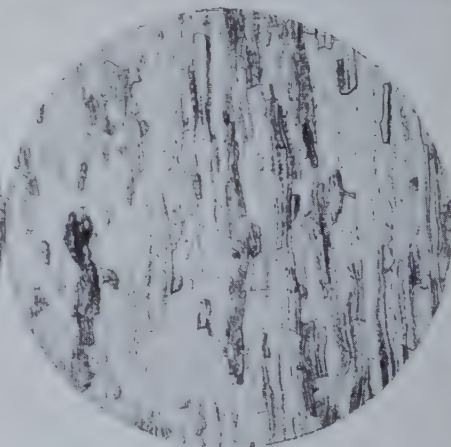


FIG. 12.

FIG. 12.—ZINC-TITANIUM ALLOY 50 PER CENT COLD REDUCTION FOLLOWED BY ANNEAL OF FIVE MINUTES AT 275°C . IN OIL. $\times 200$.

structures substantially coarser than that shown in Fig. 12. Further, it has been found that ductility and other properties

sharply reduced by cold-working was found to be largely restored by suitable heat-treatment (Table 3).

The improvement in creep resistance of the zinc-titanium alloy due to the annealing treatment and the small decrease in the zinc-copper alloy are of interest.

Annealing experiments involving a range

cold-worked fabricated articles. It was of some interest, therefore, to explore the extent of changes due to annealing in specimens representing the actual fabricated piece.

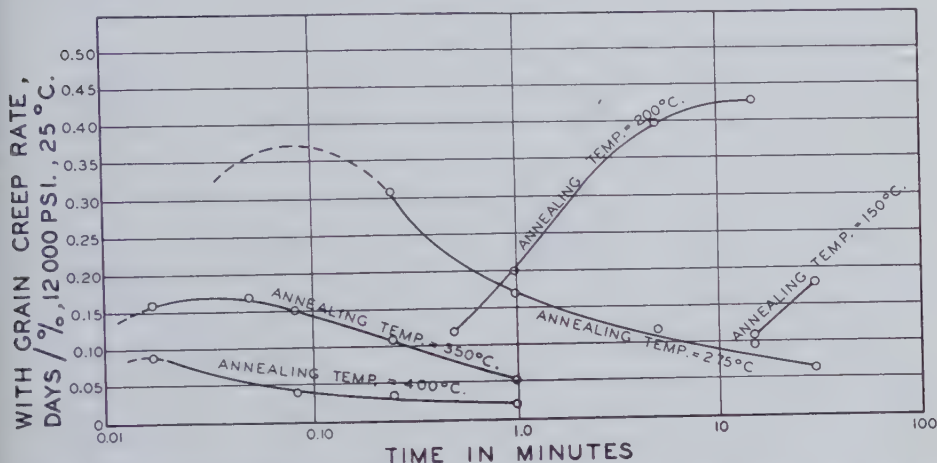


FIG. 13.—EFFECT OF ANNEALING TEMPERATURE AND TIME ON CREEP RESISTANCE OF ROLLED 0.12 PER CENT TITANIUM ALLOY AT STRESS OF 12,000 POUNDS PER SQUARE INCH.

of times and temperatures indicate that much larger improvements in creep resist-

TABLE 3.—Effect of Annealing for Five Minutes at 275°C. on Properties of Cold-rolled Zinc-titanium Alloy

Alloy	Tensile Strength, Lb. per Sq. In.		Elongation, Per Cent		Inverse Creep Rate—8000 Lb. per Sq. In., Days per Per Cent	
	As Rolled	Annealed	As Rolled	Annealed	As Rolled	Annealed
Zn-Ti	17,900	18,500	39	40	1.2	36
Zn-1 % Cu	28,000	20,400	54	49	2.3	0.95

ance are possible by the use of lower annealing temperatures (Fig. 13).

CREEP TESTS ON SPECIMENS CUT FROM DRAWN CUPS

It was realized that the decrease in creep resistance resulting from cold-rolling must also occur in drawn or otherwise

For the purpose, first-draw and redraw cups were available in sizes permitting

TABLE 4.—Creep-resistance Data on Specimens Cut from First-redraw Cups, 8000 Pounds per Square Inch

Alloy	Condition	Inverse Creep Rate, Days per Per Cent, First-redraw Cups
Zn-Ti	As drawn	4.2
Zn-Ti	5 min. at 275°C.	140
Zn-Cu	As drawn	0.18
Zn-Cu	5 min. at 275°C.	2.2

the cutting of circumferential specimens of standard size. In the early tests, specimens were cut to include, separately, the original rolling direction and the original transverse direction in the test section. Since the original grain direction seemed to have only limited influence on the creep resistance of drawn cups, all of the later work was done with specimens having the original rolling direction in the test area.

Tests of this sort furnished results (Table 4) confirming those obtained on strip; that is, low creep resistance as cold-worked and an important improvement when annealed. It seems quite feasible to produce formed articles of good creep resistance from these zinc-titanium alloys by using cold-rolled strip to facilitate drawing and relying on a final heat-treatment to attain maximum creep resistance.

STABILITY OF PROPERTIES ON AGING

Some of the curves in Fig. 13 show a decrease in creep resistance with time at annealing temperature after an initial peak has been reached. This observation caused some concern about the retention of maximum creep resistance during room-temperature and elevated-temperature service aging. Tests to explore this are being carried out on cold-rolled strip, annealed 5 min. at 275°C. Included in these tests are creep determinations at 3000 lb. per sq. in. stress at 150°C. The data to date are compiled in Table 5.

TABLE 5.—*Creep and Aging Tests at Elevated Temperature on Zinc-titanium Alloy*

Aging Treatment	Inverse Creep Rate, Days per Per Cent	
	Test at 25°C., 12,000 Lb. per Sq. In.	Test at 150°C., 3000 Lb. per Sq. In.
None ^a	0.36	4.75
1000 hr. at 150°C.....	0.52	5.74
1000 hr. at 100°C.....	0.62	4.91
1 yr. at room temperature...	0.23	5.40

^a Initially cold-rolled and annealed 5 min. at 275°C.

Any aging effect taking place during the tests to date is of insignificant consequence.

DISCUSSION OF RESULTS

The writers have no final theory to offer in explanation for the observed results cited in the paper. The restricted grain growth during annealing probably

is caused by interference of zinc-titanium compound particles rolled out into more or less continuous streaks. The peculiar brick-wall-like structure shown in Fig. 12 seems to be a result of this rolling.

The creep data, on the other hand, seem inexplicable at this time. One might hypothesize that the higher creep resistances produced by hotter rolling (Fig. 4) are associated with increased titanium in solid solution. This would explain also the loss in creep resistance during cold-rolling, which would be expected to discharge the titanium from solid solution. Likewise, resolution of titanium might be advanced to explain the improvement brought about by subsequent annealing.

This line of approach fails, however, to explain why the highest creep values were obtained at intermediate annealing temperatures (see Fig. 13) or why some of these time-temperature curves show maxima. A possible explanation might lie in a combination of solid solution stiffening of the zinc lattice with variable additional slip resistance by streaks of compound particles. Long annealing at higher temperatures might well cause sufficient coalescence of the compound particles to account for the decreases subsequent to the maxima in Fig. 13. The writers are unwilling to accept this explanation at this time.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the assistance of other members of the research staff of the New Jersey Zinc Co. in carrying out the experimental work.

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DISCUSSION

(John Ruzicka presiding)

W. L. FINK,* New Kensington, Pa.—I wonder if the author has made an effort to correlate creep with grain size in these samples. The grain size plays such an important part in determining the creep rate in other alloy systems that I would suspect that it might have the same effect here.

J. R. DAESSEN,† Hammond, Ind.—The improved creep resistance of zinc containing titanium discussed by the authors has been previously shown (John R. Daessen Patent No. 2317179, issued April 20, 1943) to be effective in zinc containing copper, in which alloys the improved creep resistance is accompanied by much greater strength and hardness than is caused by additions to zinc alone.

Similar improved creep resistances occurring at higher heat-treating temperatures are there shown to result from additions of higher-melting-point metals, which, like titanium, are sparingly soluble in the zinc-copper alloy.

E. A. ANDERSON (author's reply).—The point that Dr. Fink has raised is an excellent one. It is not one in which we have done any great amount of work. I regard it as rather significant, however, that the very coarse-grained structures obtained on the cold-rolled material subsequently annealed; that is, relatively coarse structures give superior creep resistance.

My own belief is that the matter is more fundamental than we appreciate, that nothing is known of the mechanism by which zinc creeps, and my suspicion is that this is indeed some type of combination of fact in which the

grain-growth restriction and inhibition of free motion, by the stringers of compound particles, contributes, together with matters fundamental to the relatively pure grain between the stringers, to produce these effects. But I would not argue on any theory that can be presented now. We are woefully short on facts.

Mr. Daessen's discussion is welcome. I doubt whether there is any answer we can give. It is simply a factual presentation of some information.

J. S. SMART, JR.* Barber, N. J.—Aside from the important factor of grain size, the authors have proposed that an increase in creep resistance is the result of the solution of a precipitated phase. With most metals the reverse is generally true. Have the authors considered the very likely possibility that during the stage where they are postulating solution of the precipitate they are actually obtaining precipitation, and that the increase in creep resistance may be due to the formation of this precipitate?

E. A. ANDERSON.—For zinc alloys of any importance the story so far has been one almost exclusively of solid solution. For example, in the die-casting alloys the addition of one per cent copper, which is essentially in solid solution, makes a real increase in the creep increase of the copper-free alloys, and there are many such illustrations.

I think Mr. Smart has touched on something on which we may think out loud for a moment—it might be a key to this thing—that is, the possibility that we have had precipitation-hardening within the grains. Such an effect could account for the maximum found in our time vs. temperature curves. It is a very plausible line of attack.

* American Smelting and Refining Company.

* Aluminum Research Laboratories.

† Assistant Plant Manager, Metals Refining Co. Division of The Glidden Company.

The Structure of Anodic Oxide Coatings

By J. D. EDWARDS* AND F. KELLER*

(New York Meeting, February 1944)

THE anodic treatment of aluminum presents problems of scientific as well as of commercial interest.¹⁻³ Of particular interest is the fact that, during the anodic oxidation process, the oxide continues to form at the metal-oxide interface under any oxide previously formed. This has led to speculation as to the mechanism involved in the formation of the relatively thick oxide coatings that are used commercially for decorative or protective purposes. Furthermore, the ability of certain types of oxide coatings to adsorb dyes and other substances has stimulated research to determine the actual structure of these adsorptive coatings.

It has been found that anodic oxide coatings on aluminum are composed essentially of aluminum oxide. They are formed by the action of oxygen ions penetrating to the metal surface during the electrolytic oxidation treatment. These coatings can be formed in a number of different electrolytes, as for example, those which contain sulphuric acid, chromic acid, oxalic acid, or boric acid. These are the commonest and most useful electrolytes employed commercially. Except for certain specific conditions of formation, the coatings in general have been found to be amorphous alumina, as far as can be determined by X-ray or electron-diffraction methods.

Anodic oxidation processes can be arranged in three rather general classes if they are grouped in relation to the solvent action of the electrolyte on the coating.⁴ In the first class, the electrolyte has little or no solvent action on the coating that is formed. In general, coatings produced under such circumstances are nonporous and non-adsorptive. In the second class, the electrolyte exerts an appreciable solvent action on the coating. These coatings are porous and adsorptive. Finally, for the third class, the electrolyte tends to dissolve the coating about as rapidly as it is formed. This action produces electrolytic brightening or anodic polishing of the aluminum surface and at most leaves only a very thin film of oxide.

The nonporous and nonadsorptive type of oxide film is represented by the coatings that are formed when solutions of boric acid are employed as the electrolyte. It is especially significant that these impervious films are formed in electrolytes that exert little or no solvent action on the coating. Where a boric acid electrolyte is used, the coating tends to form rapidly, with the result that the flow of current is soon reduced to substantially zero. This indicates that the growth of the coating has stopped. As a rule, the thickness of the coating is roughly proportional to the voltage employed for formation and the coatings of this type are exceedingly thin. In an electrolyte of this type, the coating has a high resistance when the aluminum is made anode; consequently, any current that may flow (leakage current) is very

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* Aluminum Research Laboratories, Aluminum Company of America, New Kensington, Pennsylvania.

¹ References are at the end of the paper.

small. Should the aluminum be made cathode, however, a substantial flow of current would occur. This asymmetric character of this type of oxide coating is utilized in electrolytic condensers and rectifiers. Several theories have been advanced to account for the unique electrical characteristics of these coatings, but these theories are beyond the scope of this paper.

Whereas the growth of a coating formed in an electrolyte containing boric acid stops when a definite thickness related to the voltage is reached, coatings made in some other electrolytes—for example, those containing sulphuric, oxalic or chromic acid—continue to increase in thickness as long as a suitable electrical potential is applied. Commercial oxide coatings formed in these electrolytes ordinarily range about 2 to 16μ in thickness. In contradistinction to the impervious type of coating, the coatings formed in the electrolytes in which the oxide has an appreciable solubility are definitely porous in character.

The existence of such pores and their size, shape and distribution have been the subject of much speculative discussion. It seems fairly certain, however, that pores play an important role in the formation, continued growth, and many other characteristics of coatings of this type. It is considered that the ability of these coatings to increase in thickness must depend upon the presence of pores of some type to carry the electrolyte from the surface of the coating close to the oxide-metal interface, so as to permit the continued passage of current. Furthermore, the fact that these coatings will adsorb dye and become colored throughout is visual evidence of a porous structure.

Rummel⁵ has estimated that the pore diameter in these oxide coatings is approximately 0.1μ . If this value is correct, the pores could not be detected by microscopic examination, since the limit of resolving power is about 0.2μ . Despite this fact, however, it has been possible by the develop-

ment of several new metallographic methods to obtain some evidence as to the character of the structure of these anodic coatings by the use of the optical microscope.

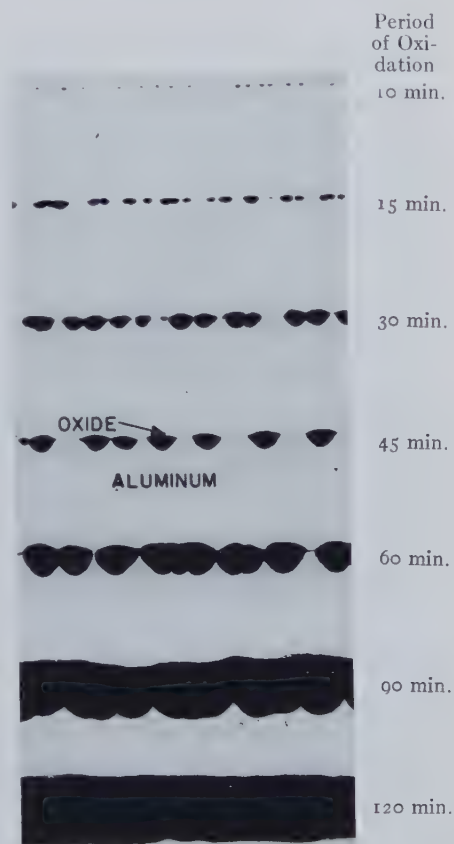


FIG. 1.—CROSS SECTIONS OF SAMPLES THAT SHOW STEP BY STEP FORMATION OF A CONTINUOUS OXIDE COATING FROM A SERIES OF ARTIFICIAL PORES SPACED 10μ APART. $\times 250$.

OXIDE FILMS AS SEEN THROUGH THE OPTICAL MICROSCOPE

By the use of these new methods, it has been possible to show in cross sections (Fig. 1) a step by step development of a continuous anodic coating from a series of artificial pores spaced about 10μ apart. The dark segments in the photomicrographs are cross sections of the growing oxide. The bottoms of these segments are roughly cir-

cular in contour and the pore center or centers are at the center of this circle. Growth of the oxide apparently has taken place radially from this center. The tops of



FIG. 2.—SURFACE SECTION OF SAMPLE SHOWING BANDS (DARK) OF OXIDE FORMED AT BASE OF CREVICES MADE IN ORIGINAL IMPERVIOUS OXIDE COATING BY BENDING SHEET. $\times 500$.

these oxide segments are not flat but are rounded and stand out in relief above the adjacent original metal surface. With continued passage of current, it is evident that the segments increase in both depth and diameter, with the ultimate result that they meet and merge into a continuous coating with a scalloped contour at the metal-oxide interface. This is shown in Fig. 1 by the cross section of the sample that had been anodically treated for 90 min. After the 120-min. treatment, both surfaces of this oxide coating appear relatively smooth and straight. This series of photomicrographs, therefore, is presented as synthetic evidence of the way in which a continuous oxide coating of substantially uniform thickness can grow from a multitude of isolated pore centers.

The artificial pores mentioned in the preceding paragraph were formed in the following manner:

A sample of high-purity aluminum sheet



FIG. 3.—CROSS SECTION OF SAMPLE SHOWN IN FIG. 2. $\times 1000$.

The segments of oxide that grew from the artificial pores show evidence of a structure radiating from each pore center.

(99.95 per cent Al) was first anodically treated in an electrolyte containing boric acid and borax, to form a thin oxide coating on the surfaces of the sample. This coated sample was then bent sharply by shearing with a pair of tin snips. The sharp bending caused the coating to craze near the sheared edges; that is, a series of very fine cracks developed in the coating parallel to the sheared edge. When this sample was subsequently immersed in an electrolyte containing sulphuric acid, and a suitable electrolytic potential was applied, the electrolyte penetrated the fine cracks in the coating and caused the growth of a small segment of oxide at the base of each of the cracks or linear artificial pores. A surface or plan view of the conformation of the oxide at the base of the cracks in the original oxide coating is shown in Fig. 2.

From the results obtained by this procedure, it is obvious that the impervious film applied first was sufficiently inert in the sulphuric acid electrolyte at the temperature employed for the second anodic treatment that it remained unattacked and acted as a stop-off. Thus, the oxidation in

the sulphuric acid electrolyte was limited to the area at the base of the cracks. Under ordinary conditions of formation of oxide coating, it is thought that the oxide would

could be revealed by the microscope, was first disclosed by Rummel. He published photomicrographs showing sections of fractured oxide coatings that had distinct

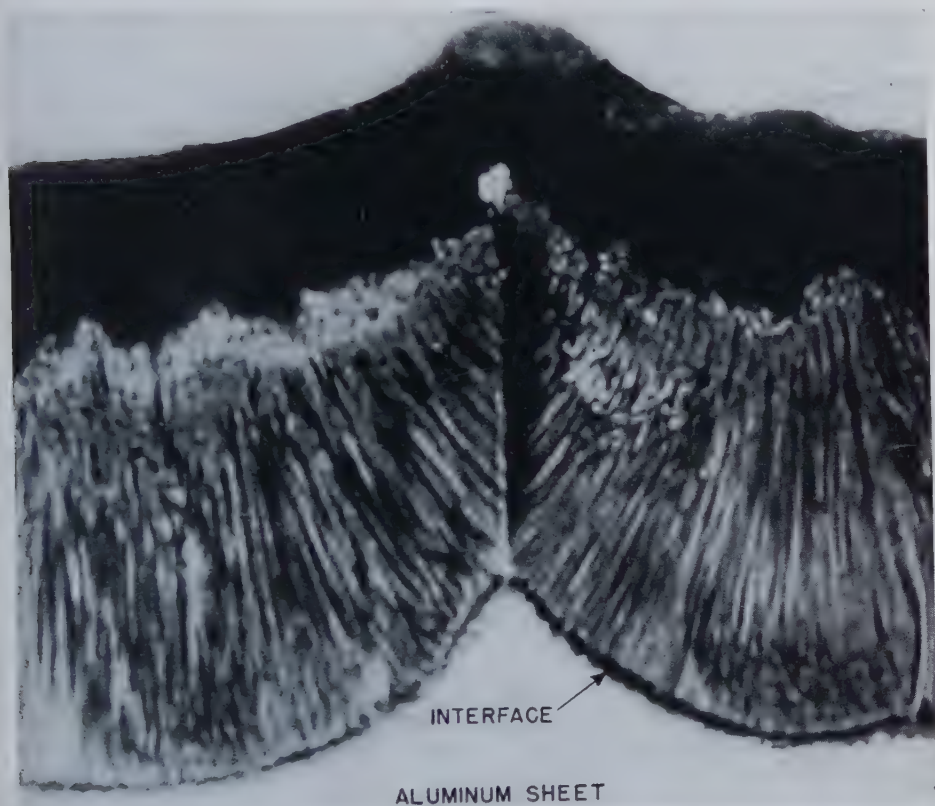


FIG. 4.—STRUCTURAL DETAILS IN OXIDE SEGMENTS AT HIGHER MAGNIFICATION.

Original magnification 2500; reduced about $\frac{1}{3}$ in reproduction.

Attention is directed to the light and dark bands and to the profile at the metal-oxide interface.

begin to form at points or on small circular areas on the metal instead of along lines. Thus the oxide formation would proceed along a hemispherical front rather than on a circular or cylindrical front as is shown. The oxide coatings on the specimens used for Figs. 1 and 2 were impregnated with potassium dichromate, to give them increased contrast of detail in the photographic reproduction.

The fact that anodic coatings might have a fine structure, some details of which

striations perpendicular to the coated metal surface. These striations were observed in coatings formed in oxalic acid but not in coatings formed in sulphuric acid electrolyte. Bauman⁶ considered that this was caused by a closer spacing of the pores and a finer structure in the latter coatings.

G. W. Wilcox, working at Aluminum Research Laboratories, found that by impregnating the porous oxide coating with potassium dichromate before preparing the usual polished cross sections

for examination, and then by employing an etching treatment after polishing, it was possible to develop a considerable amount of detail in the oxide coating. The struc-

consist of two layers—an upper layer, dark and without visible structure, and a lower layer next to the metal, which shows alternate light and dark bands more or

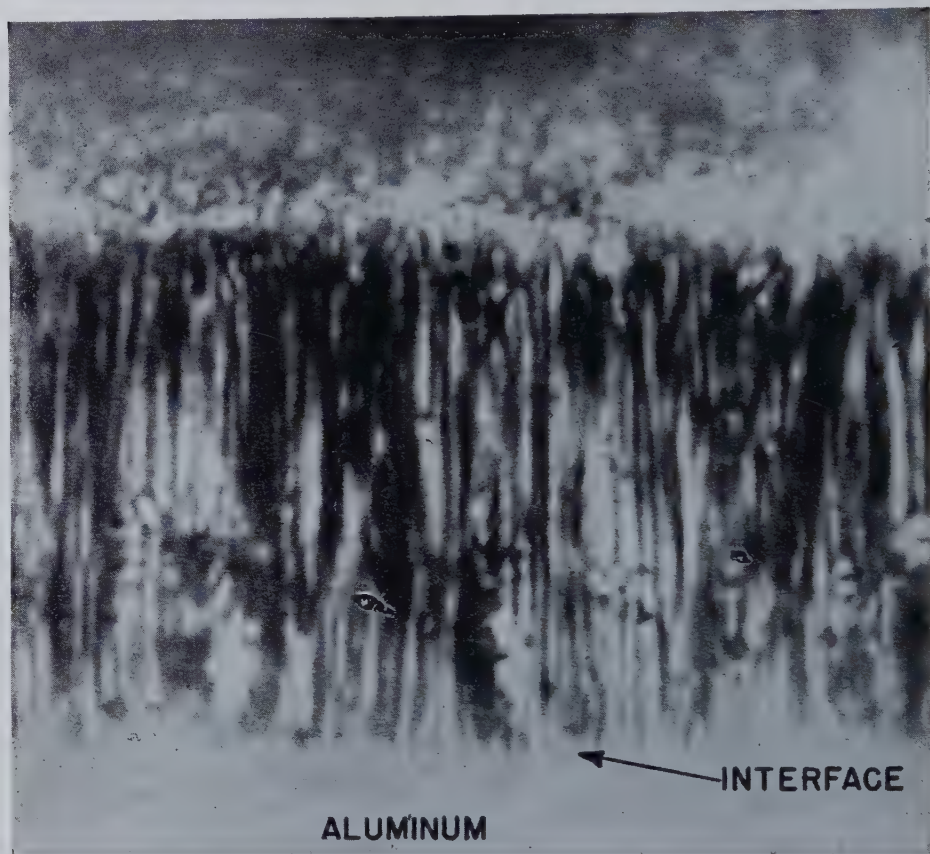


FIG. 5.—CROSS SECTION OF OXIDE COATING FORMED IN SULPHURIC ACID ELECTROLYTE BY NORMAL ANODIC TREATMENT. $\times 2500$.

The light and dark bands are normal to the sheet surface. The upper part of the oxide coating was rounded slightly in polishing; therefore, it is out of focus.

tural characteristics of such a section after etching are shown by Fig. 3. This photomicrograph shows several of the segments grown through artificial pores. The details of the structure of these segments have been brought out by impregnation with potassium dichromate followed by etching in an 0.5 per cent hydrofluoric acid solution, and are shown by Fig. 4.

The oxide coating in Fig. 4 appears to

less radially disposed toward the centers from which growth started. Closer examination reveals further details, such as small oval or circular markings in the area near the upper zone and in other areas. Near the oxide-metal interface, a darker band is evident. Just beneath this band, there appears a delicate tracery, which reveals the contour of the advancing oxide front. This is the location of the barrier

layer where the significant growth processes are taking place, but this layer is too thin to be resolved by the optical microscope. These and other details in the micro-

count of the dark bands in this photomicrograph shows that there are approximately 10,700 of these bands per centimeter at natural size. On a plane parallel to the

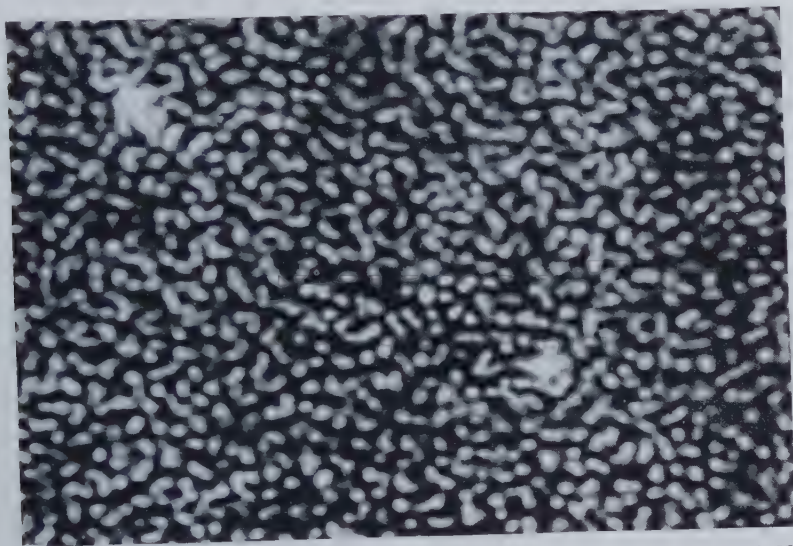


FIG. 6.—SURFACE OF ALUMINUM SHEET ANODICALLY COATED IN SULPHURIC ACID ELECTROLYTE FOR 20 SECONDS AND THEN ETCHED TO REMOVE THINNER PARTS OF OXIDE COATING $\times 2500$.

White spots are remaining areas of oxide; dark portions are bare aluminum surface. Dark-field illumination.

structure developed by etching require interpretation, which at times may be highly speculative.

Considering the bands shown in the oxide coating, the conclusion might be drawn that they indicate the pores through which the electrolyte penetrated and which subsequently were stained by impregnation with dichromate solution. A single band, however, does not necessarily represent a single pore. These bands appeared to be about 0.2 to 0.5μ wide. This same type of banded structure was observed on a sample that had received a 60-min. treatment in a sulphuric acid electrolyte, as shown in Fig. 5. On this sample, the oxide coating was formed in the normal manner instead of from artificial pores. The bands, as would be expected, are normal to the surface of the sheet. This coating also is composed of two zones. A

metal surface, at right angles to the axis of these bands, approximately $10,700^2$ or 114×10^6 bands would be intercepted per square centimeter.

It is interesting to compare some of the details of Fig. 5 with those of the surface section shown in Fig. 6, which is in a plane at right angles to that of Fig. 5. This section was prepared by polishing the surface of a piece of high-purity aluminum sheet by metallographic methods and then subjecting it to an anodic oxidation treatment for 20 sec. in a sulphuric acid electrolyte. This led to the formation of an oxide coating on the polished surface, of an estimated thickness of 0.1μ . Subsequent etching of this coated surface with a dilute hydrofluoric acid solution produced the results shown. The small white areas probably are the oxide coating remaining after the etching treat-

ment. The dark background is the metal from which most of the oxide has been dissolved. Apparently the oxide coating produced by the 20-sec. treatment was not

order of magnitude as the number of bands calculated from the examination of the cross section of the oxide coating shown in Fig. 5. These bands will be discussed

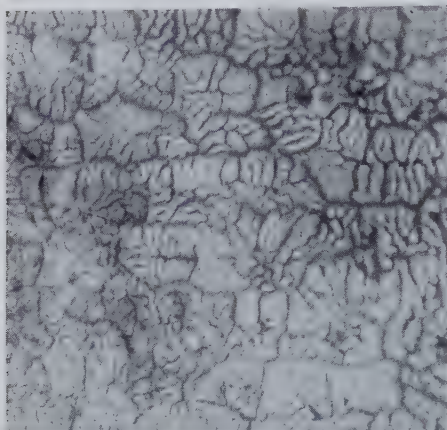


FIG. 7.—SURFACE SECTION OF OXIDE COATING FORMED IN SULPHURIC ACID ELECTROLYTE ON HIGH-PURITY ALUMINUM SHEET. $\times 1000$.

The structure is caused by solvent action of the electrolyte.

uniform in thickness. The areas remaining, therefore, are most likely the thicker parts of the oxide film. They are assumed to be the centers from which the coating started, by breakdown of the original natural oxide

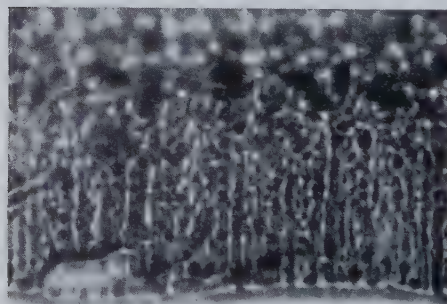


FIG. 8.—SECTION OF OXIDE COATING ON SAME SAMPLE AS FIG. 7 POLISHED AT AN ANGLE OF 45° TO SURFACE OF SHEET. $\times 1000$.

The structures in the oxide are evident. Oxide-metal interface is at bottom.

coating. An approximate count on this sample gives the number of white spots as 96×10^6 per sq. cm. This is of the same

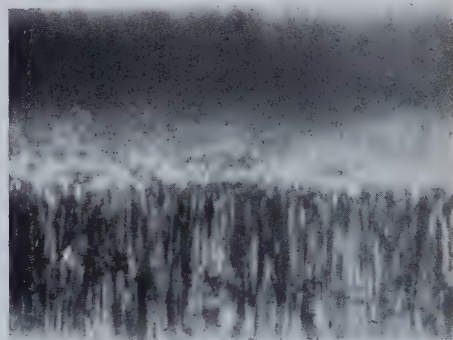


FIG. 9.—CROSS SECTION OF OXIDE COATING ON SAME SAMPLE AS FIGS. 7 AND 8. $\times 1000$.

Light and dark bands normal to sheet surface. Oxide-metal interface at bottom. Upper portion of this coating is out of focus because coating was slightly rounded in polishing.

again in the light of evidence obtained with the electron microscope.

The structure of the oxide coating shown in Fig. 4 is especially interesting. It appears to have a cellular structure composed of walls of oxide surrounding the pores or, what is more likely, groups of pores. The structure of the oxide near the surface, however, has been altered somewhat by the solvent action of the electrolyte. Partial solution of the walls of the oxide tubes has produced a spongelike structure. Further illustrations of the variations in structure from the surface of the oxide to the interface are included as Figs. 7 to 9. The first of these figures shows the structure of the oxide coating as observed on a surface section. The next shows the two types of structure developed in a cross section that was polished on a plane at an angle of 45° to the surface, and shows clearly the alteration of the outer portion of the coating. Fig. 9 shows the structure of a cross section polished on a plane perpendicular to the surface of the oxide.

OXIDE FILMS AS VIEWED WITH THE ELECTRON MICROSCOPE

Aluminum exposed to air acquires a natural oxide film that has been estimated to be of the order of 0.01μ in thickness. When aluminum is made anode in a suitable electrolyte and a suitable voltage is applied, this natural film breaks down and an anodic oxide film begins to grow immediately at a great many points on the surface. This new film is believed to grow to a limiting thickness by the interchange of aluminum and oxygen ions across the film layer, until the barrier-layer thickness of about 0.03 to 0.05μ is reached. In electrolytes in which this oxide film is not appreciably soluble, growth of the film ceases when the barrier-layer thickness is reached. For electrolytes in which the film is soluble, however, innumerable pores form in the outer face of the barrier layer by attack of the electrolyte and grow in depth as the barrier layer continues its growth into the metal. Thus the formation of relatively thick oxide films is the result of a continuation of this process, as long as the pores carry electrolyte to the barrier layer.

Although the methods so far described give some indications of the fine structure of anodic oxide coatings, it has been shown that still finer details exist in these coatings, which are beyond the resolving power of the optical microscope. This was evident when thin oxide films were used to reveal the structure of metal specimens by means of the electron microscope. The method is to apply a thin anodic coating to the metal specimen, detach the oxide film and use it as a replica of the metal surface on which it formed. This thin replica is then examined with the electron microscope. One requirement for an oxide film for this work is that it should not have a structure that will interfere with the observation of the microstructure of the metal sample.

Investigation of the characteristics of

oxide films for use as specimens for the electron microscope⁸ showed that films that are insoluble in the electrolytes in which they are formed, and that stop growing when they reach the thickness of the barrier layer, do not show evidence of any structure, even at magnifications of 60,000 diameters and higher. Films that continue to grow beyond the barrier-layer thickness, because they are soluble, do show a characteristic structure, and this structure appears to be dependent upon the composition and concentration of the electrolyte.

Anodic films formed in ammonium borate or disodium phosphate electrolytes appear structureless when viewed with the electron microscope, whereas those formed in sulphuric, chromic, oxalic, and phosphoric acid electrolytes show definite structures. The appearance of the structures of several of these films is illustrated by Figs. 10 to 12 inclusive. The pattern shown by these electron micrographs is strikingly similar to that shown in Fig. 6 but the structure is considerably finer.

An example of the development of a structure in an oxide film formed on aluminum (99.75 per cent purity) in a sulphuric acid electrolyte is illustrated by the electron micrographs shown in Figs. 13a to 13d, inclusive. The films for these illustrations were formed by anodic oxidation for periods of 3, 5, 15 and 30 sec., respectively. The coating shown in Fig. 13a, which was formed by a 3-sec. treatment, is representative of the barrier layer that is formed in this electrolyte. It does not show evidence of a structure in the coating. The coating from the sample treated for 5 sec. begins to show a structure, and those from the samples treated 15 and 30 sec. show well-developed structures in the coatings.

These coatings, which were from about 0.03 to 0.07μ , were removed from the aluminum samples by immersing the coated

Fig. 10. One-minute treatment at $7\frac{1}{2}$ volts in $7\frac{1}{2}$ per cent sulphuric acid electrolyte



Fig. 11. A 15-minute treatment at 5 volts in 1 per cent chromic acid electrolyte

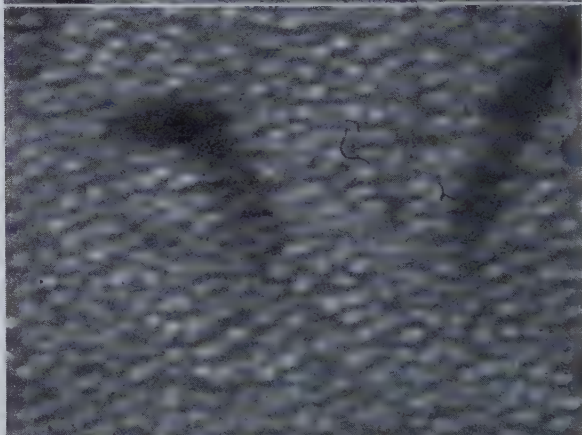
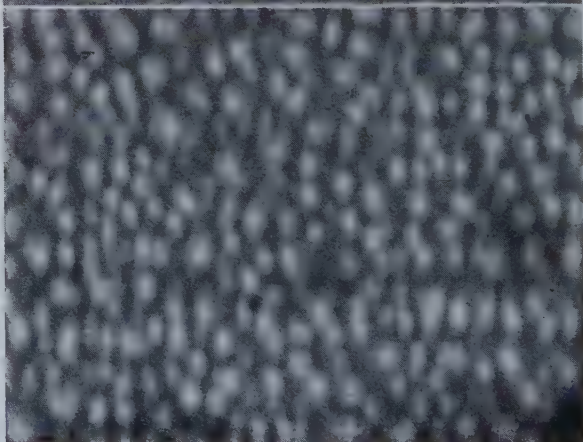


Fig. 12. A 5-minute treatment at 10 volts in 2 per cent phosphoric acid electrolyte



FIGS 10-12.—ELECTRON MICROGRAPHS SHOWING STRUCTURES OF OXIDE COATINGS ABOUT 0.05μ IN THICKNESS FORMED ON HIGH-PURITY ALUMINUM SHEET. $\times 110,000$.

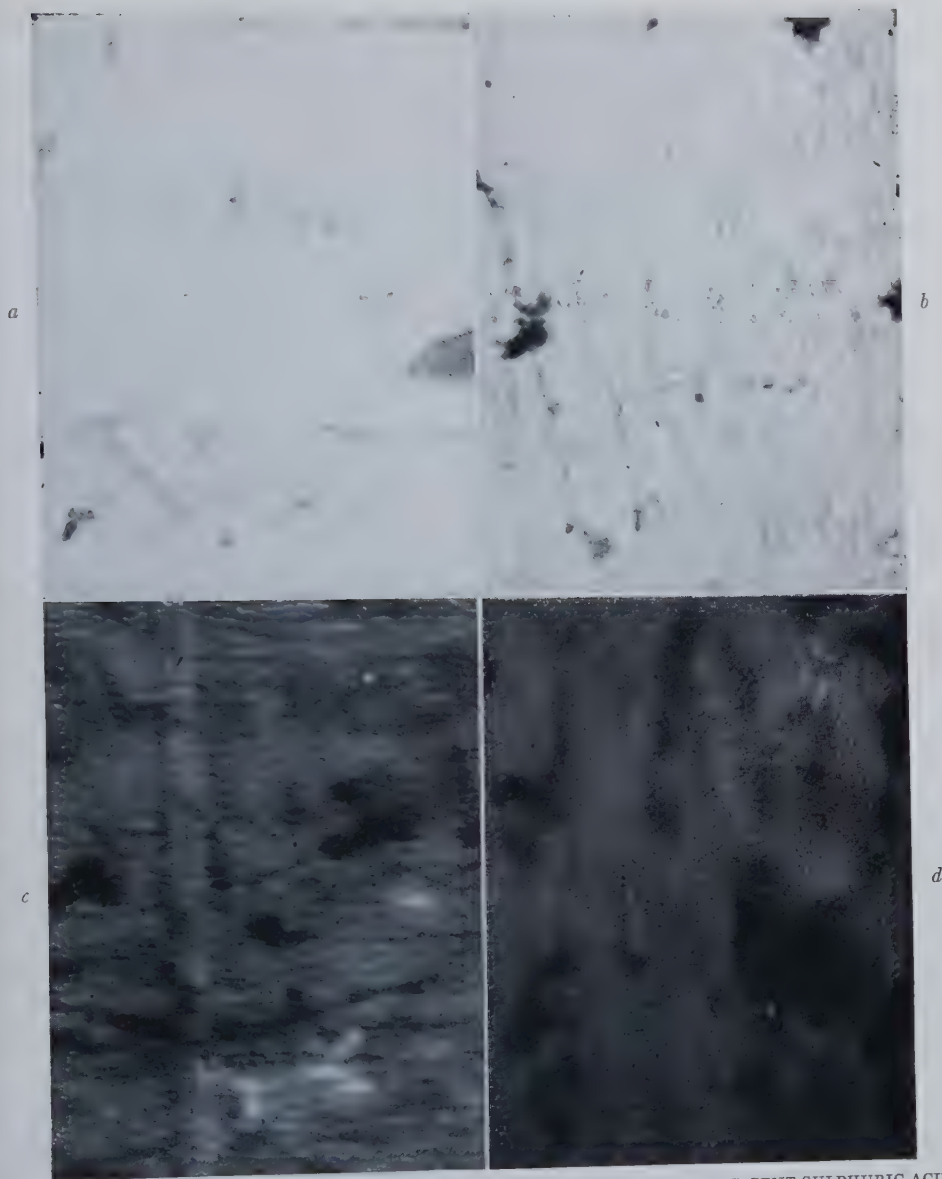


FIG. 13.—ELECTRON MICROGRAPHS OF OXIDE COATINGS FORMED IN A 15 PER CENT SULPHURIC ACID ELECTROLYTE. $\times 30,000$.

a. 3-second coating. *b.* 5-second coating. *c.* 15-second coating. *d.* 30-second coating.
The 3-second coating represents a barrier layer, which shows no structure; the others exhibit a typical structure.

samples in a saturated solution of mercuric chloride for about 30 sec. and then in distilled water. Deposited mercury dissolves the aluminum along the interface and undermines the oxide film.

silica replica, which is used as the specimen for the electron microscope, is removed by dissolving the polystyrene with ethyl bromide.

An electron micrograph of the cross

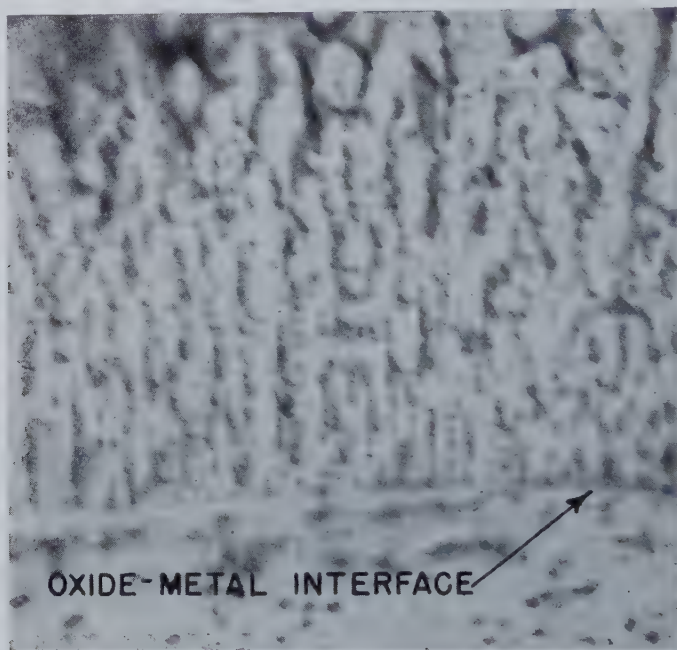


FIG. 14.—ELECTRON MICROGRAPH OF POLYSTYRENE-SILICA REPLICA OF CROSS SECTION OF OXIDE COATING MADE IN 25 PER CENT SULPHURIC ACID ELECTROLYTE. $\times 35,000$.

The vertical lines are about 0.06μ apart near interface and probably indicate pore centers from which this coating formed on the aluminum.

Since the structures of the various films were of the same type as that shown in Fig. 6 but of a much finer order, an attempt was made to obtain an electron photomicrograph of a cross section of an oxide film like that shown by Fig. 5. To accomplish this, a cross section of an oxide-coated sample, coated by the same anodic treatment as that given the specimen illustrated in Fig. 5, was polished and etched and a polystyrene-silica replica was made of the cross section.⁹ To make this replica, the polystyrene was molded against the prepared surface, then the polystyrene mold was pulled off. A film of silica was formed on this replica by evaporation. The

section of the oxide coating formed in a 25 per cent sulphuric acid electrolyte is shown in Fig. 14. The structure is of the same general type as that shown by Figs. 5 and 9 but the details are considerably finer. The dark vertical bands in this specimen are spaced about 0.06μ apart and probably indicate the location of pores from which the coating formed. It is significant also that these lines appear to get wider as they progress from the interface. This may be an indication of some solvent action of the electrolyte. It is probable that large pores form by the solution of thin walls between closely adjacent pores. The resolution at the oxide-

metal interface is not good, but there is a suggestion of the cupping action that has been mentioned previously.

SUMMARY

The use of special metallographic techniques for revealing the structure of anodic oxide coatings on aluminum has been demonstrated. With these methods considerable information about the structure of an oxide coating and the manner of its formation can be obtained. Although a characteristic structure can be revealed in an oxide coating by microscopic examination, it is evident that fine details—for example, pore size, pore spacing and profile at the metal-oxide interface—are beyond the resolving power of the optical microscope.

Data regarding the fine structure of an oxide coating have been augmented by the use of an electron microscope, which has many times the resolving power of the optical microscope. Further research is contemplated in the application of the electron microscope and other means for revealing additional details on the structure of oxide coatings and the mechanism of their formation.

ACKNOWLEDGMENT

The authors wish to acknowledge the assistance of Mr. George W. Wilcox, who worked out the various metallographic methods, and that of Dr. A. H. Geisler, who prepared the electron photomicrographs.

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DISCUSSION

(W. A. Dean presiding)

C. S. BARRETT,* Pittsburgh, Pa.—The striking thing about these optical and electron micrographs of the same coatings is the difference in the scale of the structure that is revealed. All the markings in Figs. 10, 11, and 12 are too small to be correlated with the markings in the optical pictures such as Figs. 5 and 6, except for the hazy dark markings one inch apart and upwards in Figs. 10 and 11. Could these be the dark bands of the optical pictures?

F. KELLER (author's reply).—The character of the bands shown by the optical microscope is not too definite because these bands may be associated with the stain that we use. Different thicknesses of cell walls or groups of cell walls might very well give the light and dark bands evident in the photomicrographs.

We do not believe that the bands represent in their details the same structures shown by the electron micrographs. We do feel, however, that they represent regions where the pores that are shown in the electron micrographs exist. Considering the difference in magnification—the electron micrograph at 30,000X and the optical micrograph at 3,000X—one dark band in the optical micrograph would include a considerable number of the lines that are shown in the electron micrograph. Each band, therefore, probably contains a group of pores rather than an individual pore; and if we are seeing individual pores at all they are shown only by the electron micrographs.

* Metals Research Laboratory, Carnegie Institute of Technology.

MEMBER.—Has Mr. Keller any information on how these films develop in nitric acid and can he foresee any effects in commercial corrosion?

F. KELLER.—I would like to have Mr. Edwards answer that question.

J. D. EDWARDS.—The answer is largely negative, as nitric acid is not a satisfactory electrolyte for producing these thick oxide coatings.

MEMBER.—Have you investigated the use of Alrok film by this procedure?

F. KELLER.—No, we have not. I don't think that the films produced by the Alrok (nonelectrolytic process) would lend themselves to the technique that we have used here.

MEMBER.—Have you had an opportunity to examine electroplates, and if so do they show any kind of structure?

F. KELLER.—You mean the electroplates that are produced by the process where an anodic coating is put on first and then the sample electroplated?

MEMBER.—Yes.

F. KELLER.—We are working on that problem now.

J. D. EDWARDS.—It might be interesting to have Mr. Keller tell how many pores there are per square inch in these coatings.

F. KELLER.—The number of spots on the electron micrograph of the coating made with the sulphuric acid electrolyte was 2700 per square micron; that would mean that there were 300,000,000,000 spots per sq. cm. and the number of spots on the coating made in the phosphoric acid electrolyte, the coarsest that was shown, was 500,000,000 per square centimeter.

W. A. DEAN,* Cleveland, Ohio.—Perhaps the authors can only make a guess at the answer to this question. We have been hearing about a new or super electron microscope. The talk is in terms of magnifications of 2,000,000 dia. I wonder if the authors could offer us any encouragement for the use of such an instrument in the future to reveal even finer details than they have been able to show at the magnification of this last picture.

F. KELLER.—I can give you only a tentative answer. I do not think that at this time we should be concerned about these very high magnifications. We do not have suitable methods as yet to utilize the resolving power that we can get now.

W. A. DEAN.—This has meant a great deal of development of a technique which, as Mr. Keller has indicated, needs some perfecting even now.

* Aluminum Company of America.

The Present Status of Electrolytic Manganese and Its Alloys

By R. S. DEAN,* MEMBER A.I.M.E.

(New York Meeting, February 1944)

THE commercial production of electrolytic manganese on a small scale commenced in 1939. The writer made a short report on the progress of production and utilization in MINING AND METALLURGY for January 1941. Progress during the last two years, naturally, has been more rapid.

In June 1940, Congressman (now Senator) Scrugham presented a proposal to Congress for an appropriation authorizing erection of a pilot plant for "the production of metallic manganese by electrolytic or other means." As a result of this, a pilot plant, having a capacity of a few hundred pounds per day was built at Boulder City, Nev. Subsequent appropriations permitted expansion of the plant to about a ton per day.

Much has been learned in this plant about electrolytic manganese, and the product even in its small way has found war uses of considerable importance. Meanwhile, the Knoxville plant of the Electro Manganese Corporation, the sole commercial producer, was expanded to about 4 tons per day to supply needed material for the war program. Other proposals for commercial plants have not been favorably received by the War Production Board. The Bureau reported on one such proposal by the American Alloys and Chemical Corporation.

PRACTICE AT BOULDER CITY

The present practice, as carried out at Boulder City, which is being described in more detail in a current paper by the Bureau staff at Boulder City, starts with a manganese dioxide ore containing about 20 per cent manganese. Currently this ore comes from the Three Kids deposit near Las Vegas. The steps for the production of electrolytic manganese, in general, are as follows:

1. The manganese in the ore is reduced to MnO.

2. The MnO is dissolved from the ore in spent electrolyte, which contains about 38 to 47 grams per liter of free sulphuric acid, 135 grams per liter of ammonium sulphate, and 10 to 12 grams per liter of Mn as sulphate. In the leaching step the manganese is built back up to 32 to 36 grams per liter of Mn as sulphate; the pH is adjusted to neutral by means of gaseous ammonia and passed through thickeners.

3. The electrolyte is purified by adding H_2S , which precipitates the heavy metals. After filtering, ferrous sulphate is added to the solution and oxidized with air and the solution is filtered and clarified on a precoat filter.

4. The purified catholyte is electrolyzed in a diaphragm cell using stainless-steel cathodes and lead-silver anodes. The current density is about 45 amp. per sq. ft. Current efficiencies of 60 to 65 per cent are regularly obtained.

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* Assistant Director, Bureau of Mines, U. S. Department of the Interior, Washington, D. C.

5. The brittle manganese is stripped from the cathode by bending. The stripping efficiency, in good weeks, has reached 94 or 95 per cent. The average for a year has been 82.5 per cent. Figs. 1 and 2 show the Boulder City cell room and the stripping operation.

The reduction step has been carried on satisfactorily in either a Skinner muffled-hearth furnace or a Traylor multitube furnace. With either, direct addition of oil is a satisfactory reducing agent.

Important improvements have been made in the arrangement of diaphragms. Current practice is to place the anode in the diaphragm compartment. After trials of other materials, canvas has remained the preferred diaphragm material.

The anodes of 1 per cent silver-lead gave good service, but have been replaced to some extent by an alloy of 98 per cent lead, 1 per cent silver and 1 per cent arsenic. The anodes are made in "waffle" form, with only half the surface area of the cathodes, so that anode current density is approximately twice that at the cathode, or about 90 amp. per sq. ft. Only about 1.5 per cent of the manganese deposited as metal is given off from these anodes as dioxide.

Several materials have been tried for cathodes in the course of electrolytic manganese work to date. The original work was done with 17 per cent chromium-iron. At the start of the Knoxville plant, ordinary sheet steel was used. This proved objectionable because of corrosion from spray above the solution and because of difficulty in maintaining a good surface. Aluminum was found to be a good cathode but to have erratic stripping properties. The best material found to date at Boulder City is 18 per cent chromium, 11 per cent nickel, 2 per cent molybdenum stainless steel.

Stripping is still done by manual bending and on good days 95 per cent or more of the metal is stripped. Occasional bad days still occur for stripping, but no sure cure for stripping troubles can be offered.

Quality of Product

The manganese is substantially pure, except for 0.03 to 0.07 per cent sulphur. Jacobs and Churchward, at the Bureau pilot plant at Boulder City, have established a relationship between SO_2 content of the electrolyte and sulphur content of the metal; the relationship may not, however, be a direct one.

Plating under the same conditions, except that 0.1 gram per liter of SO_2 was added to the electrolyte in one case and not in the other, the following results were obtained:

	Total S	Sulphide S
No. 1 with SO_2	0.046	0.041
No. 2 without SO_2	0.042	0.002

The increased sulphur is in the sulphide sulphur and not in the sulphate sulphur, which presumably is due to occluded electrolyte. Two further facts are of interest in interpreting this result:

1. The deposit without SO_2 was deposited as ductile gamma manganese, which remained ductile for 4 weeks.

2. The current efficiency was 60.1 per cent with SO_2 added and only 42.1 per cent without it.

The interrelation of these several factors is not at once apparent. It has been well known that manganese deposits as gamma manganese in the early stages of plating, particularly at low temperatures and high current densities. Transformation to the brittle variety, however, is a matter of hours, so that presumably the high purity of the deposit greatly slowed down the transition. It is by no means certain that the presence of SO_2 directly influences the sulphur content of the deposited metal. More probably it affects cathode current efficiency for reducing both manganese and sulphur. It is reasonable, however, to assume that reduction is easier from sulphites than from sulphates.



FIG. 1.—CELL ROOM BOULDER CITY PILOT PLANT.
Showing eight cells with the generator control panel in the background.



FIG. 2.—STRIPPING MANGANESE FROM CATHODE AT PILOT PLANT AND PACKING IT IN CARTONS
FOR SHIPMENT.

Hence we see that, while the sulphur problem in electrolytic manganese has been solved in a considerable measure, there is much interesting work to be done, in order to obtain high current efficiency, low sulphur and suitable deposits for stripping from electrodes.

The production record of the Boulder City plant, by months, for the past 18 months, is shown in Table 1.

TABLE 1.—*Production of Manganese, Boulder City Plant*

1942	Pounds	1943	Pounds
August.....	16,725	January.....	32,333
September.....	24,553	February.....	28,301
October.....	23,588	March.....	42,641
November.....	30,002	April.....	35,505
December.....	31,660	May.....	42,039
		June.....	53,705
		July.....	41,129
		August.....	25,867
		September.....	28,011
		October.....	40,619

The peak of production—approximately one ton a day—reached in June, fell off with the onset of hot weather in Boulder City. It was not possible to obtain the necessary cooling equipment to keep the electrolyte down to the required 35°C. The climb back to peak production started with cooler weather.

PRODUCTION OF ELECTROLYTIC MANGANESE

The total production at Boulder City to Oct. 1 was 517,000 lb., of which 109,000 lb. was used in magnesium-alloy bomb casings; 85,000 lb. in stainless-steel tests; 129,333 lb. was shipped to the Mint for the new nickels and 62,720 lb. to England for Lend-Lease. The remainder was used for various smaller-scale tests or is on hand.

Meanwhile, the Knoxville plant of the Electro Manganese Corporation has reached capacity production of approximately 4 tons per day, making the electrolytic manganese production capacity of the country approximately 5 tons per day.

ORE RESERVES AVAILABLE FOR MANUFACTURE OF ELECTROLYTIC MANGANESE

The future of electrolytic-manganese production obviously depends not only on satisfactory development of method but on availability of raw material and demonstration of valuable uses.

The exhaustive investigation of the manganese-ore deposits in this country, which has been carried out since 1938 by the Bureau of Mines, has not revealed great amounts of ore suitable for furnace treatment; but it has revealed large amounts of ore suitable either directly or indirectly for making electrolytic manganese. Mr. C. E. Julihn prepared, from the data available to the Bureau of Mines, the following summary of the manganese ore reserves in this country that could be used for production of electrolytic manganese.

	TONS
Manganese dioxide ore* with more than 20 per cent manganese and suitable for direct use in electrolytic manganese production; includes deposits at Batesville, Ark.; Little Florida Mountains, N. Mex.; Battle Mountain, Nev.; Wheedon, Colo.; Patagonia, Ariz.; Wickes, Mont.; Lake Valley, N. Mex.; Cartersville, Ga.; Shady Valley, Tenn.; Buckeye, Colo.; Huber Rydaldalch, Utah; and Ladd Mine, Calif.....	3,500,000
Manganese ore with 15 to 20 per cent manganese, probably requiring concentration before use; includes ore from Leadville, Colo.; Las Vegas, Nev.; Butte, Mont.; Phillipsburg, Mont.; and Drum Mountains, Utah.....	2,300,000
Manganese ore with less than 15 per cent manganese, requiring concentration before use; includes ore from Artillery	

Peak, Ariz.; Tombstone, Ariz.; Three Blocks, Nev.; Stange, Va.; Virgin River, Nev.; and Patagonia, Ariz. . .

3,600,000

Manganese ore requiring preliminary smelting or hydrometallurgical treatment; includes ore from Leadville, Colo.; Aroostook County, Maine; Chamberlain, S. Dak.; and Cuyuna Range, Minn. > 100,000,000

The extent to which concentration before leaching would be used would depend on a balance of the costs. In making electrolytic zinc, concentration is now nearly always used preliminary to leaching; for manganese, each ore would have to be studied. Data for such a study are available from Bureau of Mines ore-dressing and hydrometallurgical studies on manganese ores.

The ores listed in the last category would require some special consideration to make them usable. The nodules from the Chamberlain (S. Dak.) ore, analyzing 17 per cent Mn and 12 to 15 per cent CaO, have been used successfully at Knoxville for the production of electrolytic manganese, but the acid loss to lime is too high for good practice. The Bureau of Mines has experimented with various methods of treatment for these low-grade ores, such as matte smelting, in which the manganese is obtained as sulphide, and various hydrometallurgical methods, in which manganese carbonate or oxide is obtained.

The electrolytic manganese circuit can be somewhat simplified by using these concentrated and purified products as raw material. Whether the simplification and the lower cost of ore will justify the intermediate treatment remains to be seen. For the present, there would appear to be adequate, suitably located manganese dioxide ore to supply any foreseen expansion of the electrolytic manganese industry.

PRESENT USES OF ELECTROLYTIC MANGANESE

The New Five Cent Piece

Possibly the best known use of electrolytic manganese is as a constituent of the new five cent piece. The composition of this coin is 36 per cent Ag, 9 per cent Mn, and the balance copper. This was a compromise with the original job of congressional metallurgy, which called for 50 per cent Cu, 50 per cent Ag. The manganese is added to increase electrical resistance, so as to get the new coin past the slug rejectors. The principle on which these work does not seem to be known generally and is interesting. The coin falls down an inclined chute and bounces over a slot. If it is too light or too low in elastic modulus or elastic limit, it will not bounce over the slot and will be rejected. Thus the new nickel had to have about the same density and elastic properties as the old. To guard against other types of slugs, an alternating magnetic field is set up across the path of the coin as it rolls down the chute. If eddy currents are set up in the coin, it will be retarded, of course, in its fall and will be rejected. In order to pass the eddy current test, it is necessary that the coin have relatively high resistance; namely, 35 microhms per cm². The coin made of 50 per cent Cu and 50 per cent Ag did not have it, but the addition of manganese gave the necessary resistance.¹

The alloy made with electrolytic manganese is just sufficiently malleable and anneals at a temperature just low enough to permit manufacture in the regular minting equipment. Even the small percentage of impurities introduced by 9 per cent of furnace manganese was enough to raise annealing temperature and make minting difficult. The Mint soon learned to demand electrolytic manganese. As the Knoxville output was committed to other war uses, the Boulder City pilot plant supplied much

¹ References are at the end of the paper.

of the manganese in the early stages of the "new nickel manufacture." As stated above, 129,333 lb. of electrolytic manganese was supplied to the Mint from the

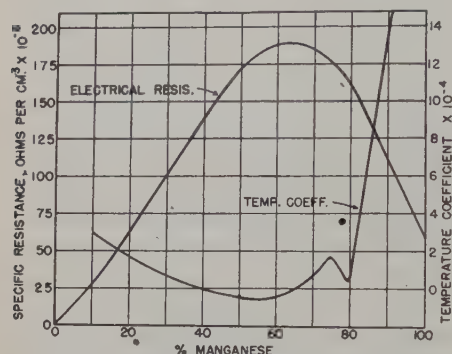


FIG. 3.—ELECTRICAL RESISTANCE AND TEMPERATURE COEFFICIENT OF QUENCHED ALLOYS OF COPPER AND MANGANESE. (Potter.)

Boulder City plant. With the increased capacity at Knoxville, the Electro Manganese Corporation has now taken over supplying the total Mint requirements.

Magnesium Bomb Casings

Most magnesium alloys contain manganese, which in the past ordinarily has been added by the use of anhydrous manganese chloride. Manganese chloride is

down, electrolytic manganese was supplied from the Boulder pilot plant. So satisfactory has been the experience in using electrolytic manganese that the Bureau has supplied more than 100,000 lb. of electrolytic manganese for this bomb-case foundry.

Aluminum Alloys

The advantages of keeping iron to a very low level in certain aluminum alloys have been emphasized in technical literature. A single example will illustrate that even a few hundredths per cent of iron, which might be introduced by using impure manganese, is very harmful. Table 2 is from the work of Wolf and Neunzig.²

A considerable tonnage of electrolytic manganese was supplied to England under Lend-Lease, principally for addition to aluminum alloys. The Bureau pilot plant furnished altogether some 62,000 lb. of manganese for Lend-Lease. Considerably greater amounts were furnished by the commercial producer.

Nonferrous Alloys

In many cases, there is an advantage in the use of electrolytic manganese as an

TABLE 2.—Loss in Weight, Strength and Elongation of Three Aluminum Alloys by Immersion in Acetic Acid (100 c.c.), Sodium Chloride (100 Grams), Water (100 Grams) for a Period of Eight Days

Loss	Alloy 5 (Si, 0.32; Fe, 0.53; Mn, 1.43; bal. Al)	Alloy 10 (Si, 0.23; Fe, 0.27; Mn, 1.53; bal. Al)	Alloy 15 (Si, 0.021; Fe, 0.013; Mn, 1.47; bal. Al)
Loss in wt., grams per sq. in.	19.6	3.84	0.44
Loss in strength, kg. per sq. mm.	24.3 to 22.0	24.5 to 23.6	23.3 to 23.5
Loss in elongation, per cent in 2 in.	8.2 to 5.1	7.1 to 6.2	10.6 to 10.1

made currently, at least in part, from ferromanganese, and its reduction with magnesium involves, of course, the chlorination of 24 grams of magnesium for every 55 grams of manganese introduced. The defense plant operated at Las Vegas found difficulty in obtaining necessary manganese chloride. To prevent a foundry shut-

addition to nonferrous alloys. Since the number of such alloys with relatively low manganese content is large, the total represents the largest current use of electrolytic manganese. In nonferrous alloys with relatively high manganese content, electrolytic manganese has been found to be very important.

Table 3 shows the very large difference in properties in some alloys when using electrolytic and other grades of manganese. Of the high-manganese alloys, the only one

and in other high-expansion uses up to about 200°C., particularly where high electrical resistivity also is desirable.

An age-hardening alloy of approximately

TABLE 3.—*Difference in Mechanical Properties of Some Alloys When Made with Electrolytic and Furnace Manganese*

A. Hardenable copper-nickel-manganese alloy, 60 per cent Cu, 20 per cent Mn, 20 per cent Ni. Annealed 1200°F. and quenched (Long-Graham)

Type Manganese	Ultimate Tensile Str., Lb. per Sq. In.	Yield Str., Lb. per Sq. In.	Elongation, Per Cent in 2 In.
Furnace.....	94-100,000	50-60,000	30-33
Electrolytic.....	75-80,000	21-27,000	45-52

B. Alpha-beta copper-zinc alloys (60 per cent Cu, 40 per cent Zn) with added manganese, as hot-rolled (Moss)

2 per cent furnace.....	57,000	30,000	14
2 per cent electrolytic.....	56,300	55,300	51
5 per cent furnace.....	52,000	34,000	6
5 per cent electrolytic.....	69,000	66,000	30

C. Iron-manganese-chromium alloys, hot-rolled, quenched from 2100°F., then cold-rolled, 10 per cent reduction in area (Moss)

Alloy, 26 per cent Mn, 18 per cent Cr, bal. Fe, carbon < 0.05 per cent			
Furnace.....	89,000	59,000	45
Electrolytic.....	85,500	81,150	43
Alloy, 12 per cent Mn, 14 per cent Cr, 3 per cent Mo, bal. Fe			
Furnace.....	128,000	51,000	16
Electrolytic.....	179,000	135,000	21
Alloy, 10 per cent Mn, 16 per cent Cr, bal. Fe			
Furnace.....	146,000	39,500	30
Electrolytic.....	171,000	146,000	31

D. Copper-manganese-zinc alloys (50 per cent Cu, 35 per cent Mn, 15 per cent Zn. Deoxidized with 1 per cent Al and chill-cast (Long and Graham)

Property	Manganese Used		
	Electrolytic	Silicothermic	Low-iron Ferro
Ultimate str., lb. per sq. in.....	69,000	45,000	50,000
Elongation in 2 in., per cent.....	32	1-2	5-1
Reduction in area, per cent.....	34	0-2	0-1
Hardness, Rockwell B.....	65	77	89

in full-scale commercial use is the high-expansion alloy with the nominal composition of 72 per cent manganese, 18 per cent copper, and 10 per cent nickel. This alloy has an expansivity of 27.5×10^{-6} per deg. C. at moderate temperatures. Its other properties are presented later in this report. This alloy is finding important uses as the high-expansion member of bi-metal strip

60 per cent Cu, 20 per cent Mn, and 20 per cent Ni is being rapidly commercialized. Its hardening range (from 80,000 soft to 180,000 hard) and fatigue strength (60,000 lb. per sq. in. for 108 cycles), are substantially greater than that of copper-beryllium. A summary of tensile and electrical properties is given in the section on Cu-Mn-Ni alloys.

Ferrous Alloys

The price of electrolytic manganese has held back the demonstration and utilization on a substantial scale of its possible advantages in steel alloys. For this reason the Bureau undertook a cooperative investigation of the use of electrolytic manganese in stainless-steel manufacture with one of the steel companies. Approximately 50 tons of manganese was used in the tests. All of the results are not yet available, but the following conclusions from the preliminary report indicate the findings.

1. The recovery of manganese in furnace additions to stainless steel was 87.8 per cent compared with 84.0 per cent for low-carbon ferromanganese and for ladle additions 89.9 per cent, compared with 72.7 per cent for low-carbon ferro.

2. There was no measurable increase in the carbon or phosphorus content of the heat.

3. In these tests the recovery of manganese was more consistent from heat to heat than when using ferromanganese.

4. Because of the convenience of handling, weighing and shoveling, electrolytic manganese and the smaller bulk and weight of the addition, the time required to prepare a heat for tapping is shortened.

The low-carbon ferrous alloys, therefore, furnish a large potential use for electrolytic manganese, awaiting only production for sale at a price that is definitely possible with a large plant.

LABORATORY STUDIES OF MANGANESE ALLOYS AND PROBABLE DIRECTION OF FUTURE COMMERCIAL DEVELOPMENT

Manganese Metal

Manganese has at least three allotropic modifications:

- α , stable up 742°
- β , 742° to 1194°
- γ , 1194° to m.p.

The alpha and beta forms are complicated cubic structures, and both allotropes are brittle.

The gamma form is face-centered tetragonal and is ductile.

The electrical resistance of gamma manganese is 63 to 65 microhms per cm^3 , and of alpha manganese, 165 to 170.

Gamma manganese is formed under certain conditions in plating which yield low-sulphur deposits as previously discussed. If sufficiently pure, its transition rate to alpha is very slow. It has not, however, been possible to preserve pure gamma manganese at room temperature by quenching. The presence of only one per cent of copper, however, stabilizes the gamma form so that it can readily be obtained by quenching.

The System Copper-manganese

The copper-manganese is the basic system for most of the nonferrous manganese alloys, and considerable effort has been made to establish its constitution.

At high temperatures, below the solidus of course, the face-centered tetragonal gamma manganese is transformed by adding copper into a face-centered cube, the parameters of which gradually change to those of pure copper. This is, therefore, a continuously changing solid solution, which at about 82 per cent manganese passes from a face-centered cube into a face-centered tetragonal lattice by a gradual decrease in one of the axes. Good agreement among the data of all investigators, including our own laboratory, is indicated.

The properties of the quenched alloys appear to be those of a continuous series of solid solutions, with a possible break in properties at the transition from cubic to tetragonal at 82 per cent Mn.

The results already published show that this is approximately correct for the electrical resistance.³ The normal looking curve for electrical resistance in Fig. 3,

showing the relationship between electrical resistance and weight per cent manganese, has a peculiarity, however. It is made up of two straight lines connected by a curve.

Fig. 3 also shows the temperature coefficients of electrical resistance in this system, taken from the results of E. V. Potter in the Bureau laboratories. These

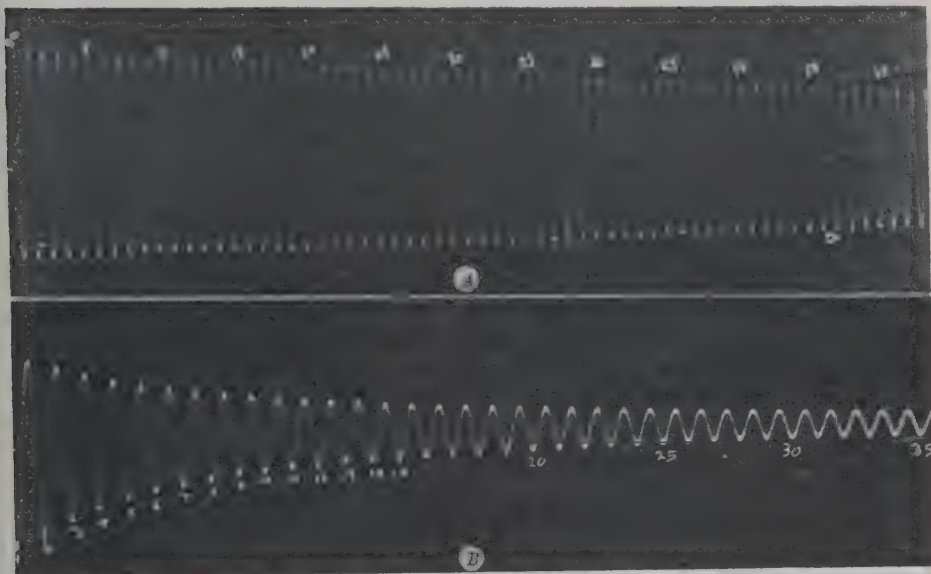


FIG. 4.—OSCILLOGRAPH RECORD OF VIBRATION IN STEEL AND MANGANESE ALLOY. (Potter.⁴)

The two straight lines terminate at 40 per cent and 82 per cent Mn, respectively. This suggests that we are dealing with two solid solutions, one of manganese in copper up to 40 per cent Mn and one of copper in manganese down to the limit of the tetragonal lattice at 82 per cent. The intermediate alloy would not appear to be so simple a solid solution.

The temperature coefficient of the quenched alloys also indicates a difference in the type of solid solution within the system. In the lower range, 0 to 40 per cent Mn, the temperature coefficient falls so as to reach approximately zero around 40 per cent Mn. It becomes negative and remains negative up to approximately 65 per cent, when it again becomes positive, but falls to zero again at about 80 per cent, when it rises very rapidly. The simpler solid solutions on both ends of the system therefore have normal positive temperature coefficients of electrical resistance.

electrical properties of the manganese-copper alloys suggest at once their use in electrical resistances; and, of course, the low-temperature coefficient of the copper-nickel-manganese alloys has long been the basis of such alloys as manganin. These alloys, however, are built around the point at which the zero line of temperature coefficient is crossed at the copper end of the system. The high-manganese end offers higher electrical resistance with equally low temperature coefficients. The 66 per cent alloy has a resistance of approximately 190 microhms per cm³, and a temperature coefficient of zero. Further, the thermal e.m.f. against copper is very low.

Next to the electrical properties of the copper-manganese alloys, or perhaps ahead of them, the outstanding characteristic of copper-manganese alloys is their vibration-damping capacity. This has been described in several publications. As a result of this extremely high internal fric-

tion, or damping capacity, the high-manganese alloys do not ring when struck. Fig. 4 shows the comparative vibration of steel and a manganese-copper alloy.

of copper-manganese alloys. An interesting use as electrical condenser plates has been described by Potter and Huber.⁴ So far no extensive commercial uses have devel-

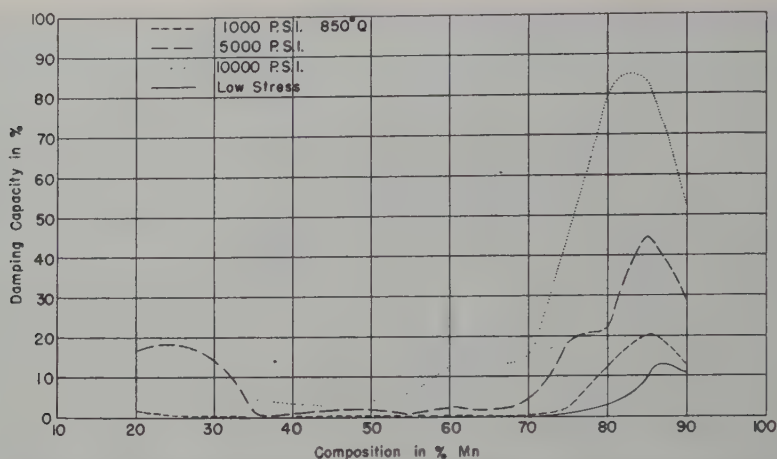


FIG. 5.—RELATION OF COMPOSITION TO VIBRATION DAMPING IN COPPER-MANGANESE ALLOYS. (Potter.⁴)

A shows the attenuation of the amplitude of vibration of a bar of steel subjected to an initial torsional stress and allowed to vibrate freely. B shows the similar attenuation of the amplitude of vibration of a bar of manganese alloy, so proportioned that the initial amplitude of vibration is very nearly the same as that of the steel bar recorded in A. The vibrations of the steel bar are more rapid, and the attenuation of amplitude with both the number of vibrations and with time, are very much greater for the manganese alloy. A comparison of the amplitudes of vibration in the two bars after 25 cycles indicates that in steel the amplitude has decreased to approximately 80 per cent while in manganese it has decreased to 20 per cent of the original amplitude. Fig. 5 shows the relationship between manganese content and damping at several stresses. Other physical properties of the 82 per cent alloy, which shows the highest damping capacity, are given in Table 4. Numerous uses have been suggested for the high vibration damping

oped. The sharp maximum of damping around 82 per cent Mn, the limit of the tetragonal lattice, is evident.

TABLE 4.—Properties of a Copper-manganese Alloy Containing 82.9 Per Cent Manganese, Balance Copper, Rapidly Cooled from 850°C.

Damping capacity at low stress, per cent.	7
Electrical resistivity, ohms per cm ² , at 20°C.	149 × 10 ⁻⁶
Density, grams per c.c.	7.16
Thermal coefficient of expansion per deg. C.	20 × 10 ⁻⁶
Tensile strength, lb. per sq. in.	68,000
Yield strength, lb. per sq. in.	24,000
Proportional limit, lb. per sq. in.	13,000
Elongation (1/4-in. gauge length), per cent.	35
Reduction of area, per cent.	49
Rockwell hardness.	B-55
Endurance limit for 1 × 10 ⁸ cycles, lb. per sq. in.	17,000
Young's modulus, lb. per sq. in.	13 × 10 ⁶

The most significant, or certainly the most unusual structure observed in the manganese-copper alloys is the so-called block structure, shown in Fig. 6, which occurs in the composition range 50 to 60 per cent Mn when heated to 700° to 850°C. and quenched. This was noted several years ago in a study of these alloys⁵ in

which an attempt was made to explain this structure as in reality an intergrowth of two very similar, but not isomorphous, phases. Further studies of this system, however, have made this explanation less probable. Meanwhile Corson⁶ published pictures of an identical "strange structure" in an alloy of copper with 1.05 per cent beryllium, which had been "overaged" at 600°C., and also in an alloy of copper with 35 per cent antimony, chill-cast and annealed at 600°C.

This structure is too definite and reproducible not to be significant. Corson makes no suggestions for its meaning, and our earlier suggestion for the copper-manganese case is not applicable to the others. The Cu-Be and Cu-Sb diagrams indicate that the structure occurs in the alloy on heating just above the temperature where the molecular attraction becomes strong enough to form the lattices CuBe and Cu₃Sb, respectively. By analogy, and for other reasons, I now suggest that the copper-manganese block structure is formed just above the temperature where the attraction between manganese and copper results in the separation of a second phase, but where such attraction is sufficient to cause the properties of the alloy to depart from the behavior of the simpler terminal solid solutions.

Behavior of Copper-manganese Alloys at Low Temperatures

The exact nature of the transitions that take place at low temperatures in copper-manganese alloys has by no means been settled. Extensive work has been done by Long and Potter in Bureau laboratories and by Prof. C. Y. Clayton at Rolla. By very slow cooling, Clayton has found a definite eutectoid structure at about 50 per cent Mn (Fig. 7).

The most complete study of the mechanical properties of the copper-manganese alloys has been made by Hesse and Myskowski.⁷ Their results, shown in

Fig. 8, are entirely consistent with the tentative diagram.

The strength of the quenched alloys shows breaks at 40 and 80 per cent Mn;

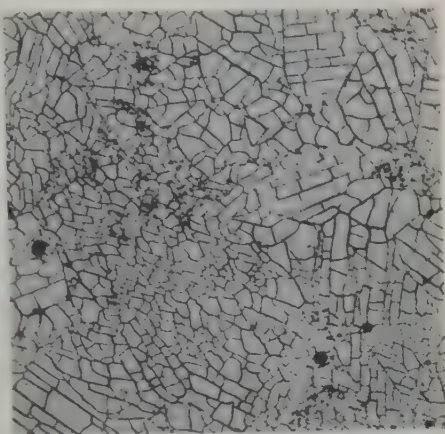


FIG. 6.—MANGANESE-COPPER ALLOY, SHOWING BLOCK STRUCTURE. (Jacobs.)

and on the alloys aged at 450°C. there is a sharp drop in both strength and ductility at 80 per cent Mn, where the diagram indicates the first separation of alpha manganese.

The System Manganese-copper-nickel

The commercial development of the high-expansion alloys and the hardening alloys in the series manganese-copper-nickel has been mentioned earlier in this paper. It seems likely that, even with these developments, the possibilities of the system have not been exhausted. The electrical resistance and temperature coefficient of the manganese-copper-nickel alloys are shown in Figs. 9 and 10.

The properties of the 72 per cent Mn, 18 per cent Cu, 10 per cent Ni alloy are shown in Table 5.

The use of the manganese-copper-nickel alloys, having a relatively low manganese content, such as manganin for electrical resistances, is well known. The possibilities of obtaining a much higher resistance, together with zero temperature

coefficient, are indicated by the data in Fig. 10.

The effect of nickel is to stabilize the copper-manganese solid solution. This is

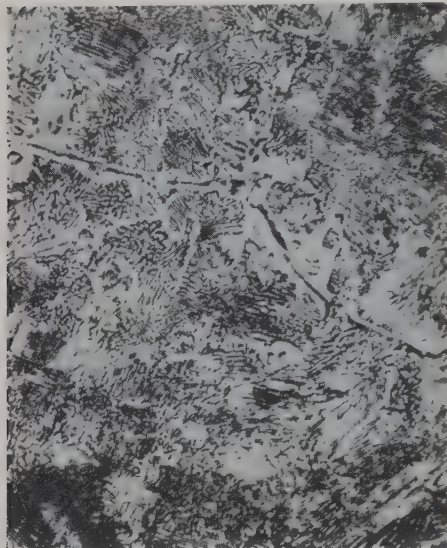


FIG. 7.—EUTECTOID STRUCTURE FOUND IN 50 PER CENT MANGANESE-COPPER ALLOY VERY SLOWLY COOLED. (Clayton.)

clearly illustrated by the example in Table 6.

TABLE 5.—Physical Constants of High-expansion Alloy

72 PER CENT MANGANESE, 18 PER CENT COPPER, 10 PER CENT NICKEL ^a	
Electrical resistivity: ohms per circular mil-foot at 30°F.....	1050
Ohms per square mil-foot at 80°F.....	825
Microhms per cm ² , at 25°C.....	175
Temperature coefficient of resistance, deg. C. (25°-150°C.).....	0.000141
Temperature coefficient of expansion (25°-150°C.).....	27.5×10^{-6}
Thermal conductivity, cal. per sec. per sq. cm. per deg. C. per cm.....	0.02
Emissivity, per cent: as rolled.....	26
As polished.....	20
Specific heat 15° to 35°C., cal. per gram per deg. C.....	0.126
Density, grams per cm ³	7.21
Weight, lb. per cu. in.....	0.26
Vibration-damping constant, per cent.....	2.3
Hardness-Vickers, 50 per cent cold reduction.....	220
Modulus of elasticity.....	18×10^6
Tensile strength, lb. per sq. in.....	115,000
Yield stress, 0.1 per cent set pounds per sq. in.....	95,000
Proportional limit, lb. per sq. in.....	50,000
Elongation in 2 in., per cent.....	6.5

^a Data submitted by W. M. Chace Co.

TABLE 6.—Stabilizing Effect of Nickel

Alloy Composition, 65 Per Cent Mn, 35 Per Cent Cu

	Temperature Coefficient of Resistance, Ohms per Ohm per Deg. C.	Specific Resistance, Microhms per Cm ² , at 20°C.
Quenched.....	+0.000004	183.2
Reheated to 450°C....	+0.0010	116

Alloy Composition, 65 Per Cent Mn, 13 Per Cent Ni, Bal., Cu

Quenched.....	-0.0000083	189.8
Reheated to 450°C....	-0.0000084	182.9

The relatively small change in the nickel alloy between reheated and quenched is notable; even more so is the close agreement in properties between the reheated nickel alloy and the quenched copper-manganese of the same manganese content.

The decrease in resistance on reheating as compared with quenching, as a function of nickel content for manganese-copper-nickel alloys, is shown in Fig. 11. The maximum nickel is required for 65 per cent alloys and is, as indicated in Fig. 11, around 15 per cent. These data permit us to plot the limit of the copper-manganese type solid solution on the ternary diagram, as in Fig. 12, which shows also the hardening range of what may be termed the Cu-MnNi type of solid solution, which can be so effectively hardened by thermal treatment. Properties that can be expected in the 60 per cent Cu, 20 per cent Mn, 20 per cent Ni alloys are given in Table 7.

There are two other types of solid solution in this ternary system, the nickel-manganese type (characterized by formation of the very magnetic, ordered lattice Ni₃Mn on heating to 450°C.) and the manganese-nickel-type solid solutions.

Magnesium Alloys

The behavior of nickel and manganese together as a hardener for copper suggested that they might produce a hardening

alloy of magnesium, and this has been found to be true. Table 8 gives a single example of these alloys taken from tests made by Cresap Moss in the Bureau laboratories.

of 1 per cent Mn, 4.5 per cent Li, balance magnesium, could be cold-worked to 60 per cent reduction in area as cast and 96 per cent after one anneal.

Adequate data are not available on the

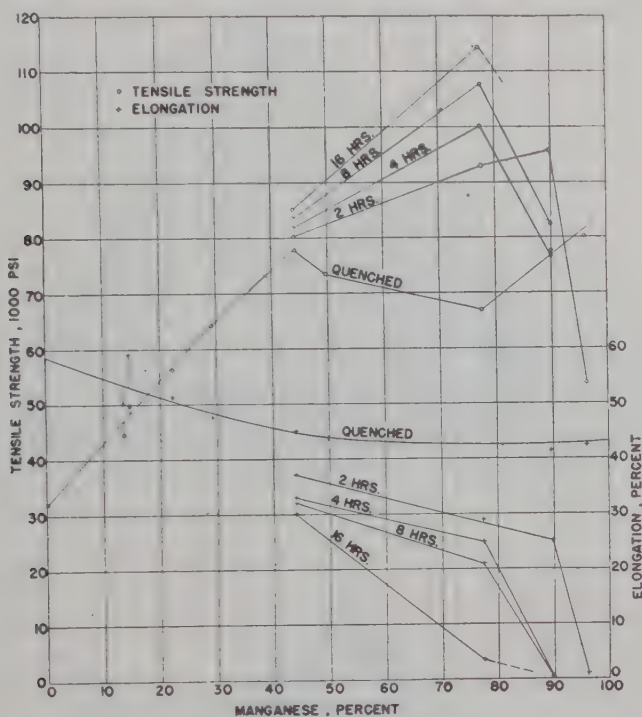


FIG. 8.—TENSILE STRENGTH AND ELONGATION OF MANGANESE-COPPER ALLOYS AS QUENCHED AND AS TEMPERED AT 450°C. (842°F.). (Hesse and Myskowski.⁷)

Other interesting series of magnesium alloys containing manganese are those to which lithium is added. Such alloys can be cold-rolled far more effectively than most magnesium alloys. A single example will illustrate their possibilities. An alloy

mechanical properties of these lithium alloys, but 40,000 lb. per sq. in. tensile strength for the cold-worked alloys appears to be easily obtainable. The effect of lithium is to considerably lower the modulus, which might be desirable for

TABLE 7.—Properties Expected in Copper-manganese-nickel Alloys
60 PER CENT CU, 20 PER CENT MN, 20 PER CENT NI

Condition	Ultimate Tensile Strength, Lb. per Sq. In.	Yield, 0.2 Per Cent Offset, Lb. per Sq. In.	Elong. in 2 In., Per Cent	Fatigue Limit, 10 ⁸ Cycles	Resistivity, Microhm per Cm ² . at 20°C.	Modulus, Lb. per Sq. In.	Thermal Expansion per Deg. C.
Soft.....	75-80,000	21-27,000	45-52				
Hard.....	180,000	160,000	2.5-3	60,000	65.5	20.95 × 10 ⁶	18 × 10 ⁻⁶

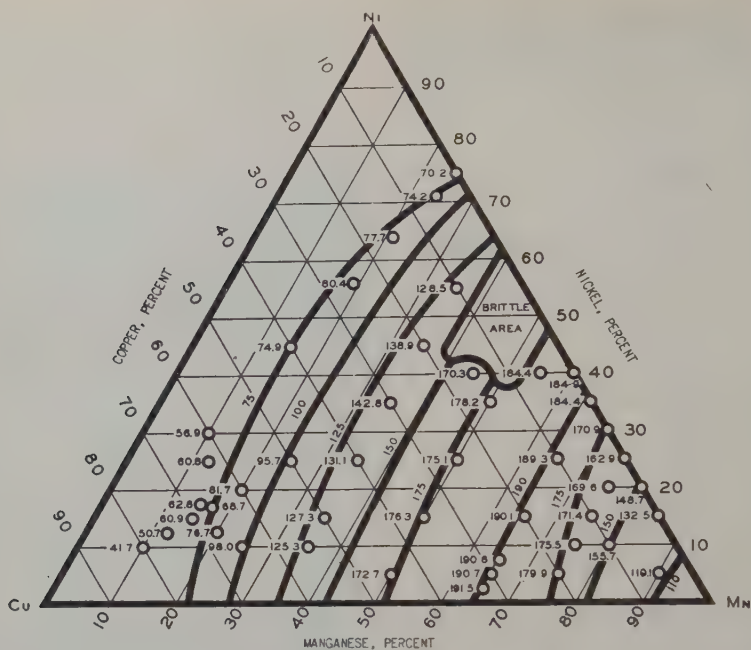


FIG. 9.—SPECIFIC RESISTANCE OF MANGANESE-NICKEL-COPPER ALLOYS. (Dean and Anderson.)
Ohms $\times 10^{-6}$ per cm^3 .

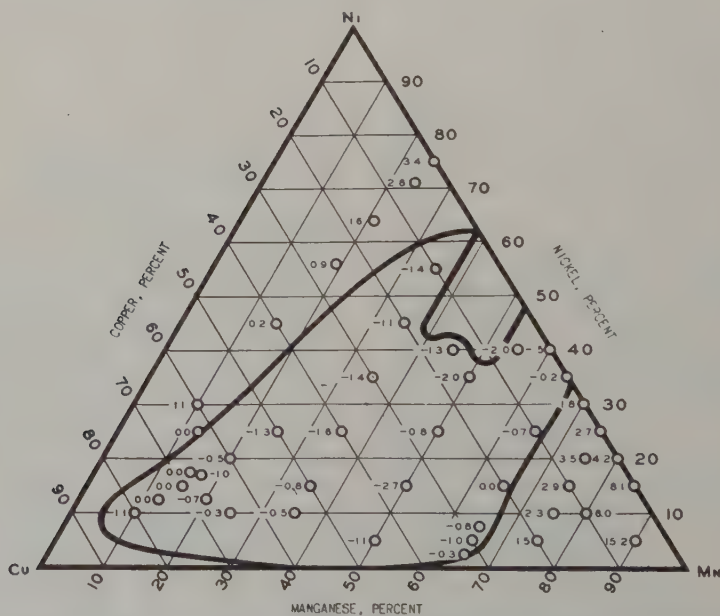


FIG. 10.—TEMPERATURE COEFFICIENT OF ELECTRICAL RESISTANCE. (Dean and Anderson.)³
Ohms $\times 10^{-4}$ per deg. C.

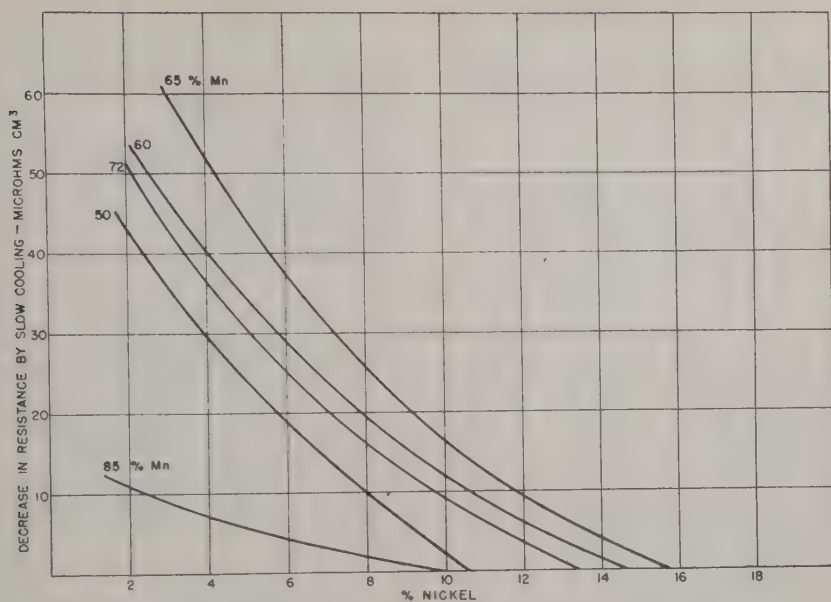


FIG. 11.—STABILIZING EFFECT OF NICKEL ON MANGANESE-COPPER ALLOYS.

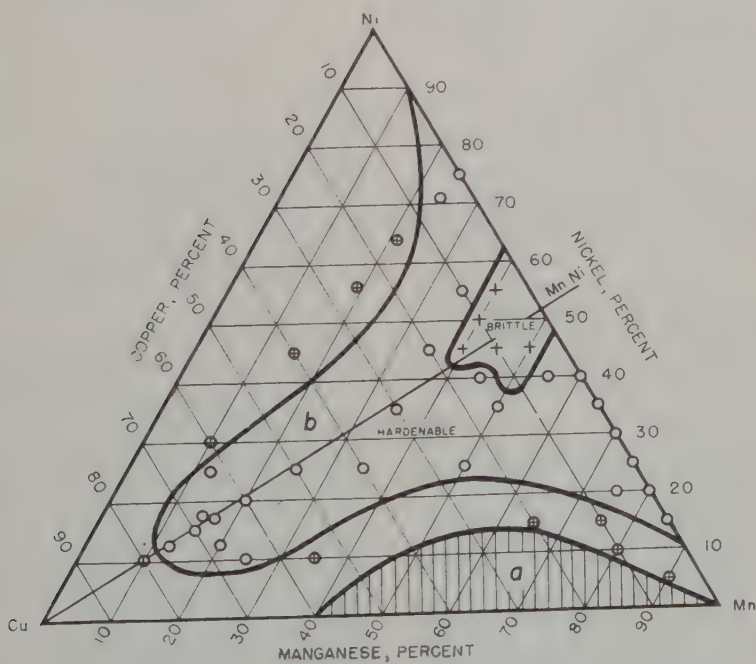


FIG. 12.—LIMIT OF COPPER-MANGANESE SOLID SOLUTION.

certain purposes such as diaphragms. The modulus of the alloy given as an example is approximately 4.67×10^{-6} lb. per sq. in. compared with about 6.8 for most magnesium alloys.

TABLE 8.—*Properties of Extruded Alloy*
4 PER CENT MG, 4 PER CENT NI, 2 PER CENT
Mn

	As Extruded	At 500°F.
Tensile strength, lb. per sq. in.....	55,000	47,400
Yield strength, lb. per sq. in.....	39,500	44,600
Elongation, per cent....	3	4
Reduction of area, per cent.....	6	0
Rockwell hardness.....	F75	F63
Electrical resistance, ohms per cm ³	8.67×10^{-6}	
Density.....	1.853	
Damping capacity, per cent.....	0.076	
Modulus, lb. per sq. in.	6.86×10^6	
Coefficient of expansion, cm. per cm. per deg. C.	0-100 24.8 0-200 26.5 0-300 27.2	

For the sake of comparison, the homogenized and hardened 10 per cent Al alloy is listed as having the following properties:

Electrical resistance ohms per cm ³	11.67×10^{-6}
Tensile strength, lb. per sq. in.....	50,000
Yield strength, lb. per sq. in.....	35,000
Elongation, per cu. ft.....	3

Both the magnesium-manganese-nickel and the magnesium-manganese-lithium alloys are less corrosion resistant than currently commercial alloys, and protective treatments must be developed.

Alloys of Copper, Manganese, and Zinc

There is little doubt that the alloys of this system will find a number of uses. The addition of manganese to copper-zinc alloys within the alpha range gives an increase in tensile and yield strength without substantial loss in ductility.

The results of tests by J. R. Long, in the Bureau laboratories, on the annealed and fully cold-worked alloys having 65 per cent Cu, 0 to 30 per cent Mn, balance zinc, are given in another paper currently released.

Alloys containing about 5 per cent Mn have nearly the same properties as 70-30

brass. Increasing the manganese, however, increases both ultimate and yield strength rapidly up to 10 per cent and less rapidly beyond that percentage.

The ductility of the annealed material falls off rapidly with manganese above 10, but elongation of the fully cold-worked material is relatively independent of manganese content.

By lowering the copper and increasing zinc a series of alloys can be obtained having many of the properties of nickel-silver. Direct substitution of manganese for nickel in the ordinary 18 per cent nickel-silver, giving a composition of 18 per cent Mn, 15 per cent Zn, 67 per cent Cu, yields an alloy having substantially the same mechanical properties as the nickel-silver.

TABLE 9.—*Properties of a 70 Per Cent Zinc,*
20 Per Cent Manganese, 10 Per Cent
Copper Alloy^a

Property	Cast	Extruded
Hardness, Rockwell C.....	7	7
Electrical resistance, ohms per cm ³		128.5×10^{-6}
Tensile strength, lb. per sq. in.....	75,000	106,000
Elongation, per cent.....	1-3	16
Coefficient of expansion, cm. per cm. per deg. C.....		25.2×10^{-6}
Vibration damping, per cent.		0.018

^a C. T. Anderson: Report of Conference on Metallurgical Research, Bureau of Mines, Salt Lake City, Utah (May 21, 1940) 129.

Increasing the manganese to 35 per cent provides an interesting series of alloys having good casting and corrosion-resisting properties. Properties of such alloys when chill-cast have been given in Table 3.

The alloys high in zinc, in the ternary series zinc-copper-manganese, need to be mentioned. Such alloys as 70 per cent Zn, 20 per cent Mn, 10 per cent Cu, may be extruded or hot-pressed and have exceptional mechanical properties. A typical example is given in Table 9.

Alloys in this series still higher in zinc may be used for die castings.

DIRECTION OF POSSIBLE FUTURE DEVELOPMENT OF FERROUS ALLOYS

In connection with the difference in properties of alloys made with electrolytic and other manganese some of the iron-chromium-manganese alloys have been discussed. These alloys, within certain ranges, have exceptional cold-rolling properties combined with resistance to atmospheric corrosion.

The mechanical properties of pure iron-manganese alloys made with electrolytic manganese have been reported by Walters,⁸ who found that, in contradiction to earlier work with impure manganese, all the alloys of manganese and iron, up to 20 per cent Mn, were ductile, and, in fact, had greater elongations with respect to their tensile strength than S.A.E. steels. Uses based on the properties of pure iron-manganese alloys can be expected.

The strongest alloy in the series contained 11.54 per cent Mn and had an ultimate tensile strength of 150,000 lb. elongation 25 to 27 per cent.⁸

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DISCUSSION

(E. M. Wisc presiding)

C. L. MANTELL,* New York, N. Y.—Have you any figures, Dr. Dean, which would allow for comparison of electrolytic manganese with other electrolytic products? That is, in terms of kilowatt hours per pound for the d. c. and a. c. power? That is the first question.

The second is: You discuss the manganese-copper alloys but with no specific mention of manganin. I had wondered whether the Bureau had done any work in connection with manganin, particularly the surface oxide effect, which is quite important in that field.

You discussed the manganese-copper-nickel system where the nickel was a stabilizer, but seemed to avoid—I do not mean to avoid intentionally—but seemed to avoid the discussion of similar systems of manganese, copper, iron and the manganese-copper-iron-chromium. The reason for the interest is that those are in the general group of the high-resistance thousand-ohm alloys and they are of very specific interest to the nickel, chromium and nickel-chromium-iron group. Every time we have made them we successfully made them down to about 0.025-in. diameter wire sizes, but that is not where they are of interest. They are of interest in wire sizes of 0.010 and below. We make the wire very nicely and then we put it on the shelves. Three months later we come back and we find the wire is not in one continuous piece but in several hundred pieces. We do not know why. Have you any thoughts that you might leave?

I want to raise the question as to any work of the Bureau in connection with the replacement of part of the nickel in nickel-silver alloys by manganese. There had been some successful work done on that.

R. S. DEAN (author's reply).—Well, of course, you have asked detailed questions, and this was not a detailed paper. Later in the meeting Mr. Knickerbocker is going to give a paper on the operation of our Boulder City plant.†

* Consulting Engineer.

† J. H. Jacobs et al.: First Two Years Operation of the Bureau of Mines Electrolytic Manganese Pilot Plant at Boulder City, Nevada, *Metals Technology*, August 1944.

Of course, all we can say about the kilowatt hours necessary to produce electrolytic manganese is to give the best results we have been able to get, and we have been gradually edging up our current efficiency. We have been able to run individual cells for weeks at a time with some 70 per cent current efficiency. And I will have to ask Mr. Knickerbocker about what the maximum is.

R. G. KNICKERBOCKER,* Boulder City, Nev.—About 3.5 kw-hr. d. c. per pound.

R. S. DEAN.—As for the comparison of that with other electrochemical and electrometallurgical processes, that is something I have been studying. But I must say that I am not in a position to give you a real comparison. I mean, if you are interested, for example, in the kilowatt-hours per ton to produce ferromanganese. I have figures anywhere from 2200 kw-hr. up to the figure that somebody gave the Federal Power Commission of six or seven thousand, which I do not believe for a minute.

Maybe Dr. Kinzel will tell us what a good figure is for the production of ferromanganese in kilowatt-hours per pound.

On other things you are in about the same position. We know pretty well what the figures are for zinc, and some things of that kind. I do not know how far we can get down, but I imagine that somewhere around 3 kw-hr. per pound is about rock bottom, because there is always going to be some hydrogen. Seventy per cent current efficiency is 20 per cent higher than we thought we were ever going to be able to get when we started with this, so I would not want to say it was the limit. A few years ago I would have said 55 or 60 per cent was about all that we could hope for.

Now, you ask if we have done any work on manganin, and the answer is, directly on the manganin part of the range, no. Because we have been more concerned with the higher manganese alloys having that zero temperature coefficient. I did not say, and probably should have said in the article, that although nickel stabilizes the alloys as far as temperature is concerned, if you run your hand over a wire made from them, and you have a sweaty

hand, the wire will break all to pieces. They will stand about two minutes of immersion in sodium chloride. I do not know exactly what the cause of this break-up is.

We found we could draw the wire down to any given size and we could preserve it by handling it entirely with gloves, literally.

That has been solved in certain ways, not by the Bureau of Mines. Unfortunately, I am not in position to reveal the solution. I think those alloys will have a place because they have such very high resistance.

Now, as for discussion of manganese in nickel silver, I think we have made all of those alloys of one kind or another. I do not believe there is much merit in leaving much nickel in them. Going the whole way gives a pretty good alloy. We thought at one time that we saw an advantage from a corrosion standpoint of having some nickel. I would not as yet want to speak positively on it, but certainly as far as physical properties are concerned you can get any property, within reason, with just a copper-manganese and zinc. Long, what do you think about it?

J. R. LONG,* Salt Lake City, Utah.—I think that is about right.

R. S. DEAN.—Those alloys are certainly adequately resistant to ordinary atmospheric corrosion. Some of the higher manganese alloys are very nice casting alloys if there is aluminum in them, up to one per cent aluminum, for example. I guess it is a little more than a deoxidizer.

It is a necessary constituent of the alloy for casting purposes.

A. B. KINZEL,† New York, N. Y.—I think Mr. Dean has done a very excellent job in this survey. He has touched a great many different applications that may materialize some day.

I am very glad that he did emphasize the two major possibilities. That is, when we have new alloys we are looking for unique properties or lower cost. The cost story has been the subject of much conversation. There is not much to say about it that has not been said, and the real story will be told by actual

* U. S. Bureau of Mines.

† Chief Metallurgist, Union Carbide and Carbon Research Laboratories.

* U. S. Bureau of Mines.

production cost and sales price as we go along through the years.

As to unique properties, the two that Mr. Dean investigated—namely, the temperature coefficients both for electrical conductivity on the one hand and for expansion on the other—are the two properties that appear in this series of alloys as sufficiently unique to warrant our getting really interested. Whether or not we can get alloys in the electrical field that are sufficiently stable and useful remains to be seen. I think we have gone a long way in that direction. Certainly that is true in the temperature coefficient work.

I was rather interested in one statement that Mr. Dean made, and I will just wind up this little discussion with a question. He said they had been supplying Basic Magnesium at Las Vegas 20,000 lb. a month of electrolytic manganese. That is a goodly amount, of course. Is that use still experimental?

R. S. DEAN.—Well, yes and no. They are paying us for it. That is a Defense Plant Corporation proposition and the Government is transferring 38¢ a pound, I believe, from one pocket to the other, so that in that sense it is not experimental. I mean, it is rather a larger amount than we would feel justified in using if it were.

However, it is experimental in the sense that, as I said a couple of times, we still do not understand all we know about the addition of electrolytic manganese to magnesium. I understand they are still using, and naturally would be using with only that amount of electrolytic, some manganese chloride. Also, there is some question as to whether it should be put in through an intermediate alloy or put in directly. I think the problem of putting it in directly is purely mechanical. If you could just have the manganese hotter than the zinc you could get it in the magnesium. If you can get it hotter than the magnesium you can put it in. It washes in. It is just a question of time.

Of course, the trouble with manganese in magnesium is not putting it in but keeping it in. If you let it solidify it comes out again. It is one of the unhappy situations. But that amount is really just something that we are supplying. It got into the picture as they ran out of chloride down there one day and to

keep the foundry going we started pushing manganese over there. We have been more or less trying ever since to stop gracefully, without success.

A. B. KINZEL.—I gather from the paper that the stainless use, which was also in rather large amounts, is likewise still experimental?

R. S. DEAN.—It is still experimental in the sense that we are furnishing manganese on an experimental basis to a number of companies particularly for stainless welding rod and similar things.

A. B. KINZEL.—What do you mean by "experimental basis"?

R. S. DEAN.—I mean without charge on the basis that they give us the complete results. And you would be surprised how everybody would rather pay for the manganese.

This one test that I referred to did consume about 100,000 lb. or so. But it is complete and that company is now, as I understand it, purchasing electrolytic manganese on the regular basis for that work and we are no longer supplying it.

R. H. BENNETT,* Minneapolis, Minn.—I think it might be interesting to give figures as to our actual output to date of metal presumably purchased by customers who are willing and able to pay and find some benefit in using the metal. These figures comprise the total cumulative product to date from the start of our commercial operations, which can be taken as about Jan. 1, 1940.

The total is about $5\frac{3}{4}$ million pounds, $1\frac{1}{2}$ million having gone to stainless steels, possibly 40 or 50 thousand included in other steels. But the bulk is in stainless. One million has gone to light metals, principally aluminum. That includes shipments, Dr. Dean, to the United Kingdom. About $1\frac{1}{2}$ million has gone to copper-based alloys; that is, alloys in which copper is the primary constituent, bronzes and brasses. About $\frac{1}{2}$ million has gone to coinage, about $\frac{3}{4}$ million to a great many miscellaneous uses, including chemical, and about $\frac{1}{2}$ million to a strategic stock pile set up by the M.R.C. This makes a total of $5\frac{3}{4}$ millions. Our actual production as averaged

* Electro-Manganese Corporation.

in the past five months of operation has been $4\frac{1}{2}$ tons a day. Dr. Dean's paper gives it as about 4 tons, but it has actually been $4\frac{1}{2}$ tons.

A. B. KINZEL.—Over what period of time was this five and three-quarters?

R. H. BENNETT.—Since the inception of commercial operation, which is Jan. 1, 1940, to date through January last. The metal is now free from allocation. For a long time it was closely controlled by W.P.B., until output was increased by expansion of our plant down there, the expansion being finished in June 1943. From that time forward the metal has been free from allocation and can be obtained in reasonable quantities. We are not going to pass order blanks around today but I can assure you the metal is available for your needs.

Dr. Dean cites the production in the Bureau of 500,000 lb. to date, and if you add to that our $5\frac{3}{4}$ million pounds you get the total amount of electrolytic manganese produced and available for industry.

H. SCOTT,* East Pittsburgh, Pa.—In the casting field, why do you go to so high a manganese content? What would be the casting character of 10 to 20 per cent manganese in copper? What is the advantage or the function of the aluminum addition therein?

R. S. DEAN.—You are speaking of the 35 per cent manganese that I mentioned?

H. SCOTT.—Yes.

R. S. DEAN.—You should ask why they put 25 per cent manganese in there. I do not think there is anything critical about it. We have made them all the way up. One group I remember had about 17 per cent manganese. We thought the 35 per cent manganese, for some reason or other, had a little better property.

What about that, Long, what is your up-to-the-minute justification? Are you still using 35 per cent manganese because we originally thought that was a good idea?

J. R. LONG.—I think that is the reason for it.

* Westinghouse Electric and Manufacturing Company.

R. S. DEAN.—Nothing critical about it?

J. R. LONG.—No, we had to settle on something and most of the work was done along that particular line. I do not see any reason for sticking to that composition.

H. SCOTT.—Is that amount of manganese protection against loss of zinc to any extent?

R. S. DEAN.—In boiling the soup, it protects against the loss of anything.

H. SCOTT.—I mean in the molten state.

R. S. DEAN.—Well, those alloys if deoxidized with aluminum are all right. I do not think that manganese particularly protects against the loss of zinc.

MEMBER.—How is it handled in remelting scrap?

R. S. DEAN.—You are getting into commercial questions. We never melted a lot of thin scrap. There is going to be a lot of manganese lost. That question is coming up because there is some scrap that is 72-18-10, and if anybody would like to use some of that scrap I can tell them where they can get it. It is obviously a new scrap material of which a certain amount can be remelted in larger pieces, and there is always a certain amount of mill scrap. The scrap problem in manganese alloys is new because there has not been any until lately.

H. SCOTT.—How about corrosion resistance relative to the manganese-free alloy?

R. S. DEAN.—Corrosion resistance relative to a brass—we thought they were a good deal better than salt spraying, and so on. I have no quantitative figures. They seem to be more like a nickel silver than a brass.

MEMBER.—How do these things behave when silver plated, particularly after hard soldering? That is the practical situation. I should think the oxidizing ability might cause some difficulties.

R. S. DEAN.—I think that has been done and done quite satisfactorily, but I do not have the details.

We have done a little work on plating. In general those alloys seem to behave very

much like nickel silver. But perhaps the tests were not such as would indicate the difficulties that might show up in a commercial application. That is very often the case. That is emphasized with all of these things, every one of them that we have gotten into. The man who tried them has gotten into a peck of trouble but he has gradually gotten out of it. I think that they can be plated.

W. M. PEIRCE,* Palmerton, Pa.—To answer Mr. Scott's question, which I take to refer to dezincification, I would say that we have tests showing that some of these alloys behave qualitatively like the corresponding copper-zinc alloys and do undergo dezincification. We do not know that this is true of all the alloys of the system nor that the effect is quantitatively the same. The corrosion resistance of the alloys is nevertheless good.

A. C. LOONAM,† Lake Charles, La.—I have done some work on alloying electrolytic manganese with magnesium. It seems to be a case of time and temperature, but particularly of getting a flux that will keep the manganese surface clean. It has a tendency to form a black coating that absolutely insulates it from the metallic magnesium. I have made alloys as high as 2.2 per cent manganese on a small scale.

I should like to ask about this magnesium-manganese-lithium alloy. You said it could be cold-rolled. Do you mean 5 or 10 per cent?

R. S. DEAN.—No, I said in the paper 96 per cent.

A. C. LOONAM.—How high do you have to go in manganese?

R. S. DEAN.—Manganese is not important, lithium is. About 4 per cent lithium for the best results. You can get some good results below that but for one of these very rollable alloys I would like to say around 4 per cent for safety, although we made some at one time

in the laboratory with 0.5 per cent that was very good.

Are you willing to say what the flux is for putting manganese in magnesium?

A. C. LOONAM.—I had a good grade of flux of approximately the same composition as Dow 230; that is, about 55 per cent potassium chloride, 34 per cent magnesium chloride, 9 per cent barium chloride, and 2 per cent fluorspar.

R. S. DEAN.—That is more or less cell feed.

A. C. LOONAM.—There is no KCl in that. Apparently the flux has to be freshly made up. I have not had as good results with the commercial material as I had with the freshly made up material. It picks up moisture on storage and that seems to be harmful.

R. S. DEAN.—Did you use finely divided manganese?

A. C. LOONAM.—About minus 20 mesh.

R. G. KNICKERBOCKER,* Boulder City, Nev.—Basic Magnesium, Inc., has been grinding electrolytic manganese to minus 10 mesh in iron disk grinders in order to prepare the metal for introduction into molten magnesium. It has reported the presence of MnO in this metal, which is believed may be formed in the grinder. It has also been reported that finer sizes of electrolytic manganese metal are produced by grinding in a liquid media, such as formaldehyde, in order to lessen the oxidation effect on the metallic particles.

A. C. LOONAM.—When I got alloying most readily, the magnesium was actually wetting the steel crucible and the steel stirring rod. The flux was doing a good job of cleaning. Unless you get that effect the manganese goes in slowly.

R. S. DEAN.—How much iron did you take in from the steel crucible?

A. C. LOONAM.—Not much.

* Chief of Research Division, The New Jersey Zinc Company.
† Mathieson Alkali Works.

* U.S. Bureau of Mines.

SYMPOSIUM ON
PRACTICAL ASPECTS OF DIFFUSION

Symposium on Practical Aspects of Diffusion

Preface

BY ROBERT F. MEHL,* MEMBER A.I.M.E.

(Chicago Meeting, October 1943)

THE purpose of a symposium, I take it, is to gather together a group interested in a common intellectual field, in order to exchange views, and to appraise the state of knowledge. Symposia are the more successful, the greater the activity in the chosen field and the wider the range of applicability of the information gained. From time to time, as emphasis changes from one field of research to another, a given subject may enjoy popularity and later retire into a scientific somnolence, for fashions change even among engineers and scientists. The subject of this symposium, however, enjoys the advantages of wide applicability and of high current interest and productivity in results. It is a timely subject for a symposium; with much new information, surely metallurgical engineers should now devote an increasing attention to its application to practice.

In beginning the symposium, I shall attempt briefly to appraise our basic knowledge in the field, to survey instances of practical usefulness, and to suggest where new work might be most productive of useful results. There are many examples of direct practical application of diffusion knowledge, and it is the purpose of the several papers in this symposium to review these. In this introduction I shall attempt to take a broad view, which, while it will but poorly serve the engineer in the solution of any given problem, may perhaps be

of some use in assessing the state of knowledge in this field.

RATE OF DIFFUSION

Liquid Metals

The process of diffusion among liquid metals, of gases in liquid or solid metals, or among solid metals, is ubiquitous, to say the least. The manufacture of alloys by the intermelting of metals, the addition of ferroalloys to molten steel, the deoxidation of molten alloys, all involve diffusion in the liquid state. The oxidation of molten copper for purposes of purification, the unsought oxidation of alloys generally during melting and casting, the reaction of liquid steel with oxidizing slags in the open-hearth furnace, the absorption of nitrogen by liquid steel, particularly in the bessemer furnace, all operate by the diffusion of gases in liquid metals.

These processes have not been studied much from the viewpoint of rates of diffusion. Alloys are made by melting metals with stirring and with allowance of time for mixing (which is diffusion) but I know of no studies that seem to define the necessary times, and though in only very rare cases can faulty properties of the finished castings be ascribed to inadequate mixing, and though certainly in most cases, with stirring, the rate of diffusion is adequate to give sufficient mixing, a more quantitative treatment would be good to have. It is not wholly certain that thorough and sufficient mixing is at all times attained, for I suspect that ferroalloy additions to steel, and that additions of aluminum to steel as a deoxidizer, especially in the sampling of steels

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* Department of Metallurgical Engineering, Carnegie Institute of Technology, Pittsburgh, Pennsylvania.

for analysis for oxygen, may not always be well mixed.

The rates that control the over-all rate of refining of steel in an open-hearth furnace comprise the rate of absorption by the slag of (primarily) oxygen from the gas, the rate of diffusion of oxygen through the slag, the rate of exchange of oxygen from slag to molten steel, and the rate of diffusion of oxygen in the steel. Even though turbulence and boiling, and convection, provide mass kinetic disturbances, information is needed on the rates of surface interchange and of diffusion—measurements are now almost entirely lacking, doubtless because of their difficulty, but they are not impossibly difficult.^{1,2} The importance of these separate processes is greater in electric-furnace melting than in the open hearth, since stirring and convection are less severe. This case is obviously somewhat analogous to the scaling of metals in gases, and a similar quantitative behavior would be expected.

Surprisingly enough, very few measurements are available on the rate of scaling of liquid metals and alloys. While this is closely analogous to the scaling of solid metals, there are some differences—for example, there cannot be a comparable orientation relationship between the scale and the metal with accompanying atom binding across the interface. It has been observed that very small amounts of added elements may provide a skin to molten metal which greatly retards loss of a volatile constituent. We may expect that the oxide scale or film on molten alloys will show complexities in composition similar to those exhibited by the scale on solid alloys. This is a field to which a worker could devote his whole career, for it is unexploited and the results of his work would be of practical interest.

Solid Metals

The reaction of gases with solid metals obviously is of practical importance, since

metals frequently must be annealed without perfect atmospheric protection, and since it is necessary to supply the engineer with metals for the construction of equipment which show minimum deterioration in use at high temperatures. A few general principles of wide utility are available; for example, the Pilling and Bedworth principle³ associating the parabolic rate of oxidation of metals like copper with the coherency of the scale maintained by the volume expansion accompanying the formation of oxide, and associating the linear rate of metals like magnesium with the cracking of the scale occasioned by the shrinking of volume on scaling; and in alloys, the principle that protection against oxidation is assisted by the addition of a less noble metal, which, oxidizing more readily than the base metal, furnishes a nearly pure skin of the oxide of that added metal, providing protection. But the phenomena accompanying the formation of external scale on alloys are exceedingly complex, particularly with respect to compositional changes, for not only is the gross composition of the scale frequently very different from that of the alloy, but usually there are differences in composition from the inside to the outside of the scale, as also of the metal.⁴⁻⁶

The parabolic rate of oxidation of metals is the result of the laws of diffusion; at a given temperature the rate of scale growth depends upon the concentration gradients of oxygen and the rate of diffusion of oxygen in the scale and in the metal, though unfortunately there have been no direct determinations of the rate of diffusion in oxides. Although such a simple analysis cannot be made for the oxidation of alloys, this is probably only because of the complexity in composition and phase relationships, and lack of information on diffusion coefficients and on solubilities.

In addition to the formation of external scales, the oxidation of alloys is accompanied by internal oxidation of the less noble constituents, a subject to which

¹ References are at the end of the paper,

F. N. Rhines⁷⁻⁹ has contributed in recent years, and, as he shows in his paper in this symposium (p. 335), the phenomenon is one of practical importance. The rate of internal oxidation, the rate of formation of the so-called subscale, may be analyzed quantitatively, at least formally, and has been demonstrated to conform to diffusion laws. The process furnishes a technique for the study of some of the more obscure phenomena of diffusion; for example, anisotropy in diffusion and the rates of grain-boundary diffusion, to which reference will be made later.

These studies on the rate of oxidation of metals and alloys have furnished much basic knowledge on the diffusion process. It is probably proper to digress here to remark that knowledge in a field advances not only by fits and starts in the usual fashion, but often by the growth of knowledge in a parallel field: ideas on the nature of diffusion in solid metals have been much extended by findings in the field of oxidation, as in another case new ideas have been obtained from such an apparently remote field as the electrical conductivity of solid salts. The metallurgical scientist had better keep his eye not only on the metallurgical journals but also on the chemical and physical journals! For example, the phase "FeO," wüstite, formed on iron by oxidation above 570°C., is a solid solution in which there are vacant lattice positions, lattice points which in a fully developed lattice would be occupied by iron atoms;¹⁰ the growth of this scale proceeds by the diffusion of iron, not oxygen atoms, through this lattice; a similar circumstance occurs in Cu₂O and other oxides. This phenomenon has led to the assumption of vacant-lattice-point diffusion—"hole diffusion"—in metals, which at least in some cases appears to have been confirmed.

Thin Films

It may be taken, then, that there are no apparent major mysteries in the formation of scales, but for thin films—films up to 2000

Å. thick—the parabolic law fails, and an exponential law is obeyed, not reconcilable in a simple way with diffusion laws.¹¹ These films, of such importance in corrosion and oxidation behavior, certainly require further study. It is possible that a new art is appearing of the deliberate creation of special surface films, for, arguing from the electrical conductivity of compounds, Price and Thomas¹² produced a method to coat silver with an invisible film of Al₂O₃ by controlled oxidation of silver containing small amounts of aluminum, which provides a high degree of tarnish resistance. I understand that this method has found but little practical application, yet the method is very promising. Practical results of this sort should appear increasingly as continued research improves our knowledge of the process of oxidation.

CARBURIZING, DECARBURIZING AND NITRIDING

Carburizing, decarburizing, and nitriding are also examples of the reaction of metals with gases with accompanying diffusion. The arts are far advanced, but it appears that continued advance in science will assist the art.¹³ It has long been known that carburizing is a process of surface absorption of carbon from carburizing gases and the inward diffusion of this carbon. The factors that control this rate, however, have been rather obscure, despite attempts at analysis. In a formal way it is apparent that there are two processes, either of which, whichever is the slower, may determine the over-all rate—namely, the rate of absorption of carbon at the surface—and the rate of diffusion inward. If the rate of absorption at the surface is the more rapid, the surface will immediately attain and retain that carbon concentration in austenite which is in equilibrium with the gas employed at the temperature chosen; and this is, of course, readily subject to simple test. Some gases, especially the hydrocarbon,

behave in this way. If this condition obtains, the course of the curve of carbon concentration away from the surface, and the variation of this with time and temperature, should be calculable with precision from the rate of diffusion of carbon. The rate of carburization should thus be determined by the equilibrium concentration at the surface and the rate of diffusion. Good concentration penetration curves in carburizing are surprisingly scanty in the literature, but some excellent curves have been obtained recently by F. E. Harris.¹⁴

Given the surface equilibrium concentration of carbon, the curve of carbon concentration should slope off to lower values toward the center of the piece, following a sagging course, as required by the probability function for these boundary conditions. Observed curves do not depart much from the theoretical, but do show a slower rate of decrease near the surface than required by theory. It has been hard to understand this in the past, and extraneous reasons have been sought, but this now appears unnecessary. The simple curve of the probability function is drawn assuming the diffusion coefficient D to be invariant with concentration.¹⁵ Measurements by C. Wells,¹⁶ however, show that D increases with increasing carbon, up to one per cent carbon, beyond which his measurements did not extend. If it may be assumed that D continues to increase and at an accelerating rate toward the limit of solubility of carbon in gamma iron, in a manner similar to that observed for the alpha solid solutions of copper,¹⁷ it will attain fairly high values at this limit, the surface concentration in the carburized piece. And such high values at these concentrations, when used with the probability function to calculate the penetration curve would provide the course observed in the experimental curve.¹⁸

Since it has been observed that D for carbon in gamma iron is unaffected by grain size, impurities, or alloying additions

in the amounts commonly used in heat-treating steels,¹⁶ it might be suspected that various steels, including alloy steels, would carburize at the same rate when allowance is made for the variations in equilibrium solubility occasioned by alloy additions, and Harris was able to show that this is indeed the case. The practical problem of carburizing has thus been very greatly simplified. Similar analyses could readily be applied to decarburizing and nitriding.

DIFFUSION OF GASES THROUGH METALS

Simple diffusion of gases through metals, in the absence of scale or subscale formation, has been studied, especially hydrogen in palladium, iron, etc.¹⁹ The paper by F. J. Norton and A. L. Marshall (p. 351) deals with this kind of diffusion.

The diffusion of hydrogen in iron and steel is of great practical importance, in pickling, and especially in the generation of flakes in steel and in their prevention. The mechanism is certainly not simple, for the absorption of hydrogen frequently creates structural disturbances—"rifts."²⁰

The diffusion of gases through metals is expressed ordinarily in terms of a permeability coefficient, which at once includes not only the diffusion coefficient but also the rates of absorption on one side of a metal septum and the rate of desorption on the other. We should have more data where these rates are separately determined and where the diffusion coefficient is properly calculated for a known concentration gradient.

Diffusion in solid metals is the chief interest of the physical metallurgist, of course. The data on this subject are far more complete.

FREEZING OF ALLOYS

It will be recognized that the freezing of alloys requires diffusion—as Miss Gayler points out (p. 372), castings of alloys could not be made without it. The separation of the initial solid phase is ac

accompanied by a change in the composition in the liquid; as freezing proceeds diffusion in both solid and liquid phases continues. If this diffusion were infinitely rapid, the frozen alloy would be homogeneous; since diffusion in both phases is characterized by finite, not infinite, rates, the cast alloy—ingot or casting—is not homogeneous; segregation occurs, creating a structure which on the gross scale shows differences in composition from outside to center and on the fine scale shows the familiar coring associated with dendritic segregation. Little can be done to control this practically, and the engineer perforce accepts this segregation as characteristic of the alloy he is casting. The casting may be subsequently annealed, and the ingot may be subsequently worked and annealed, treatments which through the operation of diffusion tend to smooth out the variations in concentration characterizing the segregation. While gross ingot segregation responds ineffectively to this treatment, because the distances over which diffusion must operate are extreme, coring does respond in many alloys. Cold-working or hot-working breaks up the pattern of segregation, tending to sharpen local concentration gradients, much assisting diffusion upon subsequent annealing. Some alloys, particularly alloy steels, are very little responsive, however, for though the segregation of carbon can be practically eliminated, the dendritic segregation of alloy elements is very unresponsive toward annealing treatments, owing, it would seem, to their characteristically low rate of diffusion. Apparently at the moment we must suffer this type of segregation in alloy steels.

HOMOGENIZATION

The quantitative treatment of the homogenization of cast alloys is analogous to that of the homogenization of mixed powders. These two cases differ only in the fact that the cast alloy possesses points of

high and low concentration with concentration gradients between, whereas in mixed powders the initial compact is a mixture of the powders of two pure metals. Homogenization in either case consists in interdiffusion with the aim of producing a homogeneous alloy. The rate of homogenization is determined by the initial concentration differences between the points of high and low concentration, the distances between these points, which together serve to define the concentration gradient, and the structural disposition and arrangement of these points.²¹

Even if the geometry of the points, the initial concentration differences, and the diffusion coefficients are all known, the time rate of homogenization cannot be calculated, for the boundary conditions are complex and a solution to the diffusion law is not available; this matter will be mentioned later. Yet in the lack of a full solution, comparative rates can be established. For mixed powders, the effect of particle size on the rate of homogenization can be calculated, by assignment of distance and concentration indices to describe the system. Since the rate of diffusion invariably follows an exponential temperature law, with a plot of the logarithm of D against the reciprocal of the absolute temperature yielding a straight line,¹⁸ and since the variation of the rate of homogenization with temperature is determined only by the variation of D with temperature, the logarithm of the rate of homogenization (expressed as the reciprocal time to obtain a certain degree of homogenization) also plots against the reciprocal of the absolute temperature as a straight line. The rate of homogenization at two temperatures thus serves to establish the whole temperature course, and this is a result of easy practical application. In passing it should be noted that no wholly satisfactory method of describing the state of heterogeneity in an alloy has as yet been proposed, though it would be extremely useful, especially in the

study of the factors affecting the hardenability of alloy steels.²²

DIFFUSION IN TREATMENT OF METALS

The examples of the operation of the process of diffusion in the fabrication and treatment of metals are exceedingly numerous and diverse. It would serve no purpose here to review them all. Generally, in any alloy where there is solid solubility and where concentration differences occur, diffusion, however limited or extensive, will obtain. I shall here only select a few examples.

The simplest case is that of clad metals, to which attention will be directed by the paper of F. Keller and R. H. Brown (p. 377) and that of A. A. Smith (p. 387), or metals heated in media which, as in carburizing, add an element to the surface, which I. R. Kramer will describe.* What has been said concerning carburizing largely applies here; when intermediate phases occur, these will be subject to simple metallographic principles already well known,¹⁵ though the rates at which these form, obeying diffusion laws only approximately, hint at some hidden, unrecognized effect.²³ The field of protective metallic coatings has been much exploited, and doubtless will be even further developed.²⁴

The loss of a volatile component metal on the heating of an alloy, exemplified by the dezincing of alpha brass, is also an example of diffusion. The calculation of the rate of loss of zinc upon dezincing from the diffusion coefficient is easy—or, conversely, the calculation of the D from the rate of loss of Zn—and this would seem to be a simple method to determine D .²⁵ Yet the results from several workers appear to vary extremely, by as much as 10^5 in the value of D , and in no case is the value satisfyingly

near to the value determined by the more ordinary method.¹⁷ This is an important problem, which should be subject to minute study.

Both of the two major types of transformation in metals and alloys—precipitation from solid solution and eutectoid decomposition—proceed by nucleation and growth, each of which requires diffusion. Diffusion science has been applied in these subjects only in an attempt to gain an increasing knowledge of the nature of the processes; it has not as yet offered much by way of results for practice. The process of age-hardening is more complicated than it was once thought to be.²⁶

The hardening process itself is now known to be related to the formation of precipitate particles, the lattice of which is coherent with the matrix; this is a matter of lattice geometry, and the extent of hardening in a given time period of aging is as much dependent upon the lattice geometry (of matrix, transition lattice and equilibrium precipitate), which provides and maintains lattice coherence, as it is upon the rates at which nuclei of precipitate form and grow.²⁷ But even a measure of the volume of the precipitate, taken as a measurement of the true rate of aging, does not give really useful data, for the volume is determined by the rate of nucleation, by the size of the nuclei, and by the rate of growth, none of which can as yet be determined.²⁸ Even if values for them were available, not much further progress would be had, for it appears clear that knowledge of the surface energies of the participating phases is required to calculate rates of nucleation and this is not available.²⁶ In the theoretical expression for the rate of nucleation as developed by Becker²⁹ the activation heat of diffusion Q is only one of the factors. The fact that a plot of the rate of aging versus the reciprocal of the absolute temperature gives a straight line (analogously to a plot of D vs. $1/T$)—a fact that at first suggested that the rate of aging

* See end of symposium.

is determined by D , and that in some cases the temperature coefficient of the rate of aging is the same as for D —must now be held to be only a rough approximation.²⁸

Careful study shows that linearity not always obtains, and any correspondence between the Q -values is largely fortuitous. The best we can do at the moment in correlating diffusion and aging rates is to point out in a qualitative sense only that aging rates increase with temperature approximately exponentially, whereas D increases precisely exponentially, and that in various systems, and speaking quite roughly, the rate of aging at a given temperature is the greater the lower the melting point of the alloy, which is also true for D . Progress in this field in the near future is likely to be restricted to the geometry of lattices, with the energetics of the process left until there have been further advances in the physics of the solid state.

The formation of pearlite from austenite is one of segregation; pearlite, composed of lamellae of alpha iron and cementite, forms from the homogeneous solid solution austenite, and thus the diffusion of carbon is required. Pearlite forms by a process of nucleation and growth. The rate of nucleation, a readily determined quantity, cannot now be calculated, for though the concentration fluctuations in austenite might be calculated adequately, the difficulty of surface energies appears again. The rate of growth would seem to be a simpler matter, for here we need only to set up the problem of the distance over which diffusion must operate, the interlamellar spacing, and provide a proper solution to Fick's law for the case, and finally, knowing D , calculate the rate of growth. But it has not been possible to solve this problem mathematically; I shall later suggest a method of attack.

Despite these limitations, a study of D for carbon in austenite has yielded some fruit. It has been shown that D does not vary with austenite grain size, and corre-

spondingly it has been observed that the rate of growth does not vary with grain size;^{16,30,31} it has been shown that alloying elements diffuse far more slowly than carbon,³² and, since in alloy steels not only carbon but also the alloying element must diffuse, alloying elements greatly decrease the rate of growth. Further progress here will depend also on new knowledge of the physics of the solid state that will permit us to calculate the rate of nucleation, and new mathematical analyses that will provide the rate of growth.

ELECTRICAL ANALOGUE METHOD

It has been pointed out several times that diffusion data cannot now be applied to many problems because of indeterminate boundary conditions under which diffusion operates and owing to a lack of a solution to Fick's law under some complex boundary conditions. The practical problem cannot be analyzed mathematically because of its complexity. There is available now, however, an experimental method of far-reaching engineering importance, which frequently can be employed in such cases. This is the electrical analogue method, as practiced by V. Paschkis.^{33,34} This method, in which Fourier's law of heat flow (termed Fick's law when applied to diffusion) is simulated in an experimental apparatus by analogous electrical circuits, with temperature represented by voltage, heat capacity by electrical capacity, and thermal conductivity by electrical conductivity, furnishes automatic records of temperature, avoiding complicated mathematical analyses. The method has been applied to many practical engineering problems with success. Its application to diffusion problems is as direct as to heat problems, for both diffusion and the flow of heat obey Fourier's law. No use has yet been made of the method in the field of diffusion in metals, but it should greatly widen the possibilities of the engineering application of diffusion knowledge.

APPLICATION OF DIFFUSION KNOWLEDGE TO PRACTICAL PROBLEMS

Applications of diffusion knowledge to practical problems fall into two categories: first, direct application, where a result of practical importance is yielded directly; second, indirect application, where knowledge of the diffusion problem yields a better understanding of the process concerned. This second type of contribution should not be held lightly, though the engineer often tends to, for knowledge, yielding understanding, bestows upon the worker a discriminating intelligence in an approach to a practical problem; and scientific facts will, conversely, prevent him from undertaking hopeless approaches to a problem,—for example, without our present knowledge of the rate of diffusion of carbon in austenite and the factors which affect it, doubtless many of us would be attempting to produce steels of more rapid carburizing power by altering the austenite grain size.

SCIENTIFIC KNOWLEDGE OF DIFFUSION

Perhaps we should then, finally, consider the state of our scientific knowledge of diffusion.

The theory of the atomic mechanism of diffusion is in rather good shape. The old difficulty in the mechanism of atom interchange on lattice points³¹ is beginning to resolve itself by the development of the "hole" theory of diffusion, which, at least in the case of self-diffusion in copper, appears to be on firm ground.^{35,36}

Our theory of the physical factors determining the value of D in various solid solutions, however, is primitive; it rests upon studies in only a few systems, and can proceed no further at the moment than to state that D is the greater the farther the solute from the solvent in the periodic table; i.e., the greater the chemical affinity between solute and solvent. These values of D are practically exclusively for terminal solid solutions; no trustworthy data have

been reported for intermediate solid solutions. To further our knowledge of the physical factors determining the value of D , since all theoretical calculations on the solid state are difficult, a more far-flung experimental attack should be undertaken—more determinations of D in more systems. This is laborious and exceedingly time-consuming, though not difficult; it is a data-gathering job, comparable to so many others in science, for which society has never provided an adequate organization, and I suspect we shall stagger along as a scattering few assume the task. It would be good to have rapid methods to determine D , so that data collecting could proceed apace, but such methods must be able to determine D at various temperatures and in variation with concentration, else they will supply average D -values of little and deceptive usefulness.

Those solid solutions that have been thoroughly studied—e.g., carbon in austenite, zinc in alpha brass—show that D varies markedly with concentration, and I suspect it may do so in nearly every case. The rise of D to very high values near the limit of solid solubility is a striking phenomenon, of uncertain meaning. The suggestion that the variation of D with concentration originates in the variation of the thermodynamic activity coefficient with concentration hardly seems acceptable on either scientific or factual grounds. We have already³⁷ seen that a high value of D near saturation is important in the practical matter of carburizing.

Our information on the effect of grain size upon D is in a very unsatisfactory state. In some cases the observed average D varies with grain size, and in others it does not.³¹ Our most complete information is on the system tungsten-thorium, of considerable importance to the physicist but of little importance to the metallurgist. Even when the effect is recognized, our conception of grain-boundary diffusion is not clear.³⁸ Is the faster rate of diffusion at

the grain boundary restricted to a grain-boundary region only a few atoms thick, or does it extend over many atoms? Is the rate at a maximum precisely at the grain boundary, falling off away from the boundary until it assumes the value of the volume diffusion? Is the rate at the grain boundary influenced by the relative orientations of the two neighboring grains, and at a maximum perhaps when this is greatest?

When there is an appreciable difference between D at grain boundaries and within the grain, a D -value measured on a polycrystalline aggregate is an average value; but it is not yet known how this average may be calculated from the separate D -values. Grain-boundary diffusion is very important, for we observe so many processes that are much more rapid at the grain boundary; for example, the nucleation of pearlite. It is possible, as Rhines points out,^{8,39} that the rate of diffusion at grain boundaries becomes increasingly greater than that within grains as the temperature falls; this suggestion is important, and there should be much work done on it. Rhines' method of employing internal oxidation to detect this difference, though qualitative, offers a promising approach.

Nor is there much information on the anisotropy of diffusion. Our only good quantitative data are for self-diffusion in bismuth, and we need similar data for metals and alloys of commercial usefulness. While it appears that diffusion should be isotropic in cubic metals⁴⁰ qualitative observations on the diffusion of copper in aluminum suggest an anisotropy;⁴¹ this is practically of importance, for if it were general the preferred orientations of worked and recrystallized metals must be taken into account in applying diffusion data. It is possible that the anomalies in the rate of growth of intermediate phase layers mentioned earlier may be associated with such an anisotropy, though grain-boundary diffusion and grain reorientation may also be operative. The problem of anisotropy

can best be attacked by employing single crystals—indeed, far too little work on diffusion in single crystals has been attempted. Such work would yield information quite free from the ambiguity which so frequently attaches itself to work on aggregates, in which anisotropy and grain-boundary diffusion are associated in an indeterminate mixture. Related to diffusion in metals with preferred orientations, the effect of cold-work on D requires much further study; there have been no quantitative measurements. The difficulty, of course, lies in technique, since heating to provide diffusion to a degree that can be measured destroys cold-work; it is necessary to measure D at very low temperatures, requiring the special techniques of electron diffraction or radioactive tracers.³¹ It would be pleasant to have a plot of D versus percentage cold-work.

This field is one of the important fields in metallurgical engineering and science. Knowledge of diffusion can solve practical problems directly, and has done so, and it has increased and will continue to increase understanding in many fields apparently unrelated. If it is true, as I sometimes think it is, that the profession of metallurgy suffers a bit from a sort of schizophrenia—half science and half engineering—we should try to alloy these halves more completely, with really good science anxious to minister to really good engineering, and with good engineering freely demonstrating its interest and its debt to good science.

I think we shall continue to face the necessity of developing much of our own basic science, for while physicists and chemists have contributed much to metallurgy, any study of the history of the main branches of the science of metals discloses that the workers directly or indirectly allied to the metal industries have contributed by far the more; but we must be busier at developing our science of metals, and we must do much better work. And our

engineering should be more independent of other branches of engineering, attempting to create a true branch of modern engineering out of its present science and its present practical information. Engineering and science—both of these are our responsibility.

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The Influence of Gas-metal Diffusion in Fabricating Processes

BY FREDERICK N. RHINES,* MEMBER A.I.M.E.

(Chicago Meeting, October, 1943)

BECAUSE of the nature of the environments in which metals are handled, it is natural that gases should be suspected of intruding into metallurgical operations, there to produce effects both beneficial and detrimental. The problem of tracing and controlling such effects is often made difficult by the complexity of the conditions surrounding their occurrence, even though the fundamental mechanisms involved may be simple and of familiar type. Many gas-metal reactions are known to be implemented by processes of diffusion. These form a homogeneous group of phenomena which become more readily understandable when viewed together, in that the knowledge gained from one serves to interpret the next.

It is the purpose of the present paper to present, by means of examples drawn from practice, a brief survey of the ways in which gas-metal diffusion serves and obstructs the purposes of the metal-fabricating industries. The selection of the cases described was made by consulting more than thirty-six practicing experts whose combined experience provided an extensive coverage of the field and who were in a position to supply examples of occurrences of present day interest. The

response was generous and it is regrettable that space permits the description of only a limited number of typical examples with but brief mention of parallel cases.

THE NATURE OF GAS-METAL DIFFUSION

The term "gas-metal diffusion," although commonly used, is ambiguous in so far as it implies that a definite group of substances may be identified as gases and may be expected to behave in a manner distinct from other substances in association with metals. "Gases" such as oxygen and hydrogen when diffusing through a liquid or solid metal are properly components of the liquid or solid solution; they behave as alloying elements and are not to be distinguished in their diffusion characteristics from other elements, except that each has an individual rate of diffusion. On the other hand, a number of metals in certain temperature ranges are volatile to the extent that they may appear in the form of vapor in metallurgical operations. For the sake of greater definiteness, therefore, it will be convenient to regard as "gas-metal diffusion" any process in which the result depends upon one or more of the diffusing elements appearing, at some stage, in the gaseous state, or as a compound gas.

No element, gaseous or otherwise, can diffuse through a liquid or solid metal unless it is at least slightly soluble in that metal. The elements of low atomic number

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* Assistant Professor and Member of the Staff of the Metals Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa.

such as hydrogen, oxygen, and carbon are believed to diffuse interstitially; they have relatively high rates of diffusion in the metals in which they are soluble. This is the one characteristic that may be said to set the "gases" in a unique class as regards diffusion behavior.

It is highly improbable that any substance can diffuse through a solid in the molecular form.¹ Such diatomic and polyatomic gases as H_2 , O_2 , CO , CH_4 , must dissociate when they enter the metal and reassociate upon being expelled. Consistent with this view is the observation that deliberately dissociated gases are absorbed by metals much more rapidly than are initially molecular gases and the saturation limit is much higher.*

As the degree of dissociation of a gas increases with the temperature, the rate of its absorption by the metal increases correspondingly.

The rate of diffusion of a gas into a metal rises likewise with the partial pressure of the gas up to the dissociation pressure of the first stable compound that forms (thereafter it increases only if the gas is soluble in the compound); this is equivalent to saying that the amount diffused increases with the concentration head where the maximum head is that provided by the solid solution in equilibrium with the compound. Rates of diffusion are also subject to the accelerating or retarding influence of alloying elements and to increase by cold-work.

These principles will be found to apply in all of the cases about to be described; the

more specialized characteristics of "gas-metal diffusion" will be pointed out as the need arises in connection with individual processes.

GASES IN MOLTEN METALS

It is generally observed that liquid metals become "gassed" more rapidly when overheated.* Accelerated "gassing" at high temperatures may result from one or more of several causes: (1) greater solubility of the gas, (2) more rapid diffusion, or (3) a greater portion of the gas in the atomic rather than the molecular state. Increased solubility has probably been overemphasized as an explanation of "gassing"; much of the experimental evidence on gas solubility limits is open to question upon the basis of false equilibria. On the whole, it appears more likely that accelerated gas absorption is the result of more rapid diffusion and, in some cases at least, of the presence of gases in the more active atomic form, capable of dissolving beyond the stable solubility limit.

Hydrogen is absorbed in significant quantities by almost all of the common metals except those of the "white metals" class. Moreover, most metals appear to absorb hydrogen more rapidly from water vapor than from hydrogen gas itself; presumably, nascent hydrogen is released in contact with the metal when a metal oxide is formed by the oxygen of the water molecule. Thus the presence of water vapor is perhaps one of the most common causes of the "gassing" of metals. There is a centuries old saying among bronze founders to the effect that "sound castings cannot be made when it thunders." The implication is clear, that humidity causes "gassing." Sometimes epidemics of "gassy" metal in the foundry occur in periods of

¹ References are at the end of the paper.

* Ballati and Lussana² and others have shown conclusively that nascent hydrogen produced at the outside of an iron pressure vessel will diffuse through the iron into the chamber against a high pressure of contained molecular hydrogen and still further raise its pressure. When the atomic hydrogen leaves the iron at the inside of the chamber it reassociates to molecular hydrogen (H_2) and atomic hydrogen (H^+) does not accumulate. Thus a diffusion gradient favoring the inward diffusion of atomic hydrogen is maintained.

* In this connection the term "gassing" will be understood to apply to the absorption of substances that may be released as gases at the time of freezing.

low humidity, but when related to weather conditions over an extended period are found to follow at more or less regular intervals after periods of excessive inclemency. The explanation in such cases may be that ingot stored in imperfectly protected places acquires an adsorbed film of moisture, or corrosion product, which is released, or decomposed, some time later when the ingot is melted. Preheating the ingot in an open place before melting sometimes reduces "gassing."

The noble metals, particularly silver, may be "gassed" in similar fashion by oxygen; exposure to air either dry or moist will introduce significant quantities of oxygen into silver. Nitrogen appears to dissolve in detectable though relatively small quantities in liquid metals of the iron group and, indeed, in most of the metals of the higher periods. There is some reason to believe that nitrogen may be involved in the "gassing" of iron itself, but there is scant information with regard to other metals commonly handled in the foundry.

Analyses of the gases extracted from a number of metals have tended to show the presence of a wide variety of gases. These observations, so far as they may be applied to the production of porous castings, should be accepted with reservations. Considering the existing mass of published observations as a whole, it appears reasonably certain that each metal is subject to appreciable "gassing" by a very limited number of gases. Thus aluminum probably is not sensitive to gases other than hydrogen; copper to gases other than hydrogen and sulphur dioxide, and so on. In this connection it should be observed that compound gases appear to be absorbed only when both component elements are individually soluble in the metal to an appreciable extent.

Degassing of Liquid Metals

For the removal of dissolved gases from metals, there are two common methods,

which clearly involve diffusion of the gas. The first of these, "fluxing" with an insoluble gas, is illustrated by the practice of bubbling chlorine through aluminum to remove hydrogen. A large area of oxide-free metal surface is provided by the chlorine bubbles and the hydrogen back pressure within each bubble is very low. Thus a hydrogen concentration gradient is provided between the hydrogen-rich metal and the hydrogen-poor atmosphere of the bubble and the contaminating gas diffuses out of the aluminum. Any gas, except one carrying hydrogen, that does not form a reaction film on the aluminum may be substituted for the chlorine, but oxygen and air are inferior, because the aluminum oxide film formed provides a barrier to the outward diffusion of the hydrogen. The fact that appreciable quantities of gas are removed from aluminum in a few minutes by this method provides striking evidence of the rapidity of the diffusion of hydrogen in molten aluminum.

A second method of removing dissolved gases involves slow freezing with stirring. Gas solubilities generally fall to low values abruptly at the freezing point of the metal; the major part of the gas is concentrated by diffusion into the residual liquid and eventually is evolved when the saturation limit is exceeded. It is not absolutely essential that the metal be frozen *slowly* or that it be stirred meanwhile; the soluble gas content of most metals may be materially reduced simply by double melting where the only special precaution taken is to avoid overheating and preventable access to contaminating gases during the final melting operation. Secondary metals, if free from moisture and corrosion products, often yield less "gassy" castings because they have been melted twice. Apparently, a gas such as hydrogen released as bubbles in the first freezing cycle assumes the molecular form and is not quantitatively reabsorbed during remelting, but largely escapes from the molten bath.

GAS EVOLUTION IN CASTINGS

The manner of release of dissolved gases during the freezing of a casting is subject to wide variation, depending upon: (1) the constitution of the gas-metal system, (2) the gas concentration, (3) the presence or absence of nucleating surfaces and (4) the rate of freezing. Where the metal becomes supersaturated above the melting point, gas bubbles may appear in the liquid, but their initiation is unlikely except at nucleating surfaces such as particles of floating solid matter or mold walls. Some of the gas so released may rise to the top and escape; bubbles forming on impervious mold walls more often remain as "surface blows." In the copper alloys industry, in particular, it is found that a stream of molten metal flowing down the side of the mold deposits large gas bubbles, which grow with the quantity of metal passing over a particular area of mold surface. For this and other reasons it is found best to introduce the stream of molten metal in such a way that it does not flow down a side of the mold. Excess gas, if released in the melt, is then in a more favorable position to escape.

Where the quantity of gas dissolved by the melt is initially below the saturation limit it is not evolved until sufficiently concentrated in the residual liquid by the partial freezing of the melt. The solid generally has a lower capacity for dissolving gases than has the liquid; as crystals form, the gas is rejected and becomes concentrated at the liquid-solid interface, establishing a gradient which promotes its diffusion into the remaining body of the liquid. Ultimately the saturation limit is reached and gas bubbles are formed upon nucleating solid surfaces. The physical effects of such release of gas in a partly frozen mass differ widely, dependent upon the quantity of gas released and upon the geometrical forms of the openings among the crystals.

If the quantity of gas is large and it is released before a bridging network of solid has formed, much of the gas may escape through the top of the casting, occasional bubbles being caught under overhanging ledges of solid. A familiar example of this is to be found in the rimming action of unskilled steel ingots. Carbon and oxygen concentrated in the liquid just in advance of the growing crystals are released in the form of carbon monoxide gas, which largely rises to the top of the ingot. A small part of the carbon monoxide is trapped beneath dendrite arms of columnar crystals growing into the melt all along the surfaces of the ingot and remains in the form of elongated horizontal gas pockets in the solid metal.

A large volume of gas released after an extensive network of solid has formed may result in the behavior variously known as "spitting," "sprouting" or "throwing a worm." The gas trapped within the network of dendrites increases in pressure until it drives some of the last remaining liquid out through the nearly solid upper surface of the casting. Instances of this kind of action are met where silver has been gassed with oxygen or where copper has been overpoled and contains an excess of sulphur.

Smaller quantities of gases usually act to modify the natural shrinkage behavior of the metal. It is possible to have the volume of released gas exactly compensate for the shrinkage experienced by the metal during freezing. When this occurs it is usually found that the gas tends to decentralize shrinkage and forms minute bubbles well distributed through the solid. Flat-top wirebar of tough-pitch copper is made by carefully adjusting the oxygen and sulphur content of the metal so that the critical amount of gas is present. It has also been found that difficult permanent mold castings of aluminum and sand castings of certain copper alloys, particularly those of the silicon bronze type, can be made by controlled gassing; when adequate risers

cannot be used, shrinkage may sometimes be reduced by carefully overheating the metal until it is gassed just to the necessary extent.

Under other conditions small quantities of gases appear to exaggerate interdendritic shrinkage. Apparently gas accumulating in shrinkage cavities prevents further feeding of liquid metal into the opening. This often results in the formation of long chains of interconnecting voids. Normally such voids are not open to the external surface of the casting, but when the surface is cut away in dressing or machining the casting they are uncovered and the metal is found to be porous in a pressure test.

It is interesting to reflect that, although most kinds of ingots contain some gas, either in microshrinkage cavities or in blowholes, sound wrought products can usually be made from the ingot. In many cases, the pores appear to weld completely during working and the gases vanish. Perhaps this should be expected as a result of the high rate of diffusion at hot working temperatures, the increase in pressure caused by compressing the cavities and the fact that the gases present are likely to be those that entered initially by diffusion through the metal and therefore should be capable of diffusing out again. This seems to argue that blisters in wrought products must be caused either by the presence of insoluble gases (perhaps carried in during pouring) or by the segregation of soluble gases in pockets too large to permit escape by diffusion or in which an obstruction to diffusion, such as an oxide film, has appeared.

GASES IN SOLID METALS

To a limited extent the "gases" present in solid metals are those absorbed at the time of melting and not evolved during freezing; there is ample opportunity, however, for the further introduction of "gases" in the course of the many and diverse heating operations to which metals

are subjected in the course of fabrication. It is possible, under special conditions, to introduce gases even at room temperature. In general, the capacity of solid metal to dissolve gas is less than that of the liquid and the diffusion rate is slower, but the effects produced are by no means correspondingly less significant.

Hydrogen

As with liquid metals, hydrogen is absorbed in solid metals most rapidly when supplied in the dissociated form. Thus high temperatures, the presence of water vapor or its equivalent, the release of nascent hydrogen by chemical reaction, as in pickling or electrolysis, all promote contamination with hydrogen. The practical results of hydrogen absorption, in the absence of other reacting substances, arise chiefly from its influence as an alloying element (which differs greatly from metal to metal), from volume changes and from effects associated with the subsequent evolution of gas.

Perhaps the best known of these is the hydrogen embrittlement of ferrous materials. This is encountered chiefly upon the exposure of the metal to nascent hydrogen at or near room temperature. When the source of contamination is removed, the gas gradually diffuses out of the metal and the original ductility is largely recovered; heating in the absence of hydrogen hastens the return to normal properties. A few examples of typical occurrences of hydrogen embrittlement may be of interest.

Certain high-carbon steel springs intended for use in aircraft are zinc or cadmium plated to improve their corrosion resistance. Both during preliminary electrolytic cleaning and during plating, hydrogen ions are set free at the metal surface. A considerable quantity of hydrogen is dissolved and the springs are rendered subject to failure if it is not removed before they are put into service. To accomplish its removal, the plated

springs are heated in the air at 190°C. for three hours.

Similar embrittlement often is caused simply by pickling ferrous materials. Acids such as hydrochloric and sulphuric release at the metal surface nascent hydrogen, which is partly absorbed. Where pickling occurs prior to a working operation the consequent embrittlement may be troublesome. Wire and rod pickled after an intermediate anneal must be allowed to stand in the air for some time or must be baked at a low temperature to recover ductility. Langdon and Grossmann³ have reported that embrittlement caused by pickling increases with the carbon content in hardened steels, decreases with the carbon content in normalized steels, and increases with cold-work and with the temperature of the pickle bath; ductility returns, although not completely, in about three days at room temperature. It would seem from this that the inward diffusion of hydrogen is more rapid the smaller the carbon content, but that hydrogen is a more effective embrittling agent in the unstable (hardened) material. This coincides with the common observation that low-carbon steels lose their brittleness spontaneously with greater ease than do the high-carbon steels.

Electroplates, particularly those of iron, nickel and chromium, if formed under conditions where a considerable quantity of hydrogen is released, are often very brittle and give trouble in buffing. Hydrogen probably is only a contributing cause of the excessive hardness in such cases, but whatever the cause, it is found that the ductility can be improved by baking at moderately low temperatures.

It has been suggested above that hydrogen is not completely removed by standing at room temperature or by baking. Actually, small quantities of hydrogen may remain in steels even after short treatments at relatively high temperatures, and this small residue may have a pro-

nounced influence upon the behavior of the metal. It has been shown that the elongation and reduction of an area of a 0.20 per cent carbon steel can be increased by aging at temperatures up to 540°C., and the improvement is attributed to the further escape of hydrogen.

Where ferrous materials are subjected to stress at elevated temperatures, the presence of dissolved hydrogen promotes the development of cracks. Thus hot-formed products contaminated with hydrogen are slowly cooled to avoid the development of shatter cracks. Flakes in wrought steel are believed to result from the development of fine cracks in the metal when it is worked without first being freed of hydrogen by sufficiently prolonged heating.

Some other metals are similarly sensitive to hydrogen embrittlement. Electrolytic nickel, as produced, contains a considerable quantity of hydrogen, which is partly retained through subsequent melting and casting operations if special precautions are not taken. When such nickel is rolled or forged, cracks develop. It is found possible to eliminate the major part of the hydrogen in melting by oxidation or by a carbon boil.

Tantalum is also notably embrittled by hydrogen; in this case, the gas is rapidly absorbed from heat-treating atmospheres. Since an oxidizing anneal is impractical, because of the ease of oxidation of tantalum, a vacuum treatment is used for the removal of the hydrogen.

Palladium dissolves the largest quantity of hydrogen of any of the better known metals and is somewhat embrittled thereby. It is known that a hydride of palladium is formed. Presumably the inherent brittleness of this phase is responsible for the change in properties suffered by palladium in a low-temperature hydrogen anneal.

Another effect of the diffusion of hydrogen into a metal is a small but definite increase in volume. The potential impor-

tance of this is probably not yet fully appreciated. Palladium expands as much as 4 per cent when saturated with hydrogen; iron expands somewhat less, but the results can be important. For example, electrodeposits of iron are subject to exfoliation (spontaneous peeling) if formed in the presence of excess hydrogen. It is postulated that the first layers of the iron plate laid down before the polarization of the electrolyte is fully developed are relatively low in hydrogen. Subsequent layers are more contaminated and the hydrogen contained in them tends to diffuse into the purer layers. This expands the metal first deposited without a corresponding increase in the dimensions of the outer layers, causing the plate to break away in curled flakes. Several other metals are likewise subject to exfoliation, perhaps from the same cause.

These observations lead one to wonder whether the increasing application of bright-annealing treatments will not lead to new troubles in the form of the slight distortion of some products. Possibly the distortion of sintered powder metal compacts results in part from unequal hydrogen absorption.

The electrical and magnetic properties of some metals are known to be slightly affected by the presence of dissolved hydrogen. Such effects are normally inconsequential, because the hydrogen is lost upon standing in the air; but in certain applications, such as the use of thermocouples in a hydrogen atmosphere, the results may be troublesome. It has been reported that Chromel-Alumel thermocouples may give readings as much as 100°C. low after heating for some time in moist hydrogen at 1000°C.

The release of hydrogen from solid solution is held responsible for a number of undesirable occurrences in the metals industries. Pinholes in tinplate are thought at times to be caused by bubbles of hydrogen released from the steel by accel-

erated diffusion when the metal is heated in the tin bath. Coatings of paints and enamels have been found to blister when hydrogen is released beneath them. There are other possible explanations of some of these effects, which will be mentioned presently.

It has also been suggested that blisters in wrought steel and aluminum products may be caused by the release of dissolved hydrogen acquired in pickling or in a furnace atmosphere. Presumably the gas bubble is initiated by a stress concentration, and diffusion is accelerated by the deformation of the metal. The evidence upon these points is by no means clear.

Alloys that contain oxygen, carbon, or stable hydride-forming elements are subject to chemical reaction with hydrogen. The oxygen-hydrogen reaction will be discussed in a later section. When iron-carbon, tungsten-carbon and nickel-carbon alloys are heated to a relatively high temperature in the presence of moist hydrogen, some methane gas (CH_4) escapes; in this way carbon is lost from the alloy. Decarburization is primarily a surface reaction where the carbon diffuses toward the outside and there unites with the hydrogen to form methane. Special note should be made of the importance of moisture in the system; this is another illustration of the greater activity of atomic hydrogen.

The importance of controlling heat-treating furnace atmospheres to prevent the decarburization of steels is so widely recognized that this subject may be passed over without further comment. It is perhaps not so generally appreciated that other types of alloys containing carbon are similarly subject to deterioration by decarburization; this is especially true of nickel-carbon alloys in which the temper varies with the carbon content and is therefore subject to the effects of decarburization. In some cases decarburization is desired. Moist hydrogen atmospheres can be used to purify iron, thus increasing the

magnetic permeability and affecting other properties sensitive to small quantities of carbon. Magnetic irons are sometimes treated in this way; likewise nickel for vacuum tubes may be freed of its carbon by hydrogen treatment.

Hydrogen under pressure is seldom encountered in fabricating operations, but is common in the chemical industries. Inglis and Andrews⁴ have shown that at slightly elevated temperatures (250° to 450°C.) hydrogen at 250 atmospheres pressure produces the same effects of decarburization, deoxidation and crack formation noted at lower pressures, but at more rapid rates characteristic of reaction at higher temperatures. The "caustic embrittlement" of boilers probably results from the diffusion into the steel of hydrogen under high pressure released by some reaction between the metal and water or impurities in the water.

Surface Oxidation

With a few exceptions, the surface oxidation of pure metals proceeds either by the diffusion of oxygen through the oxide layer to meet and react with the metal or by the reverse process, in which the metal diffuses outward through the oxide layer to meet the oxygen. The chief practical results of the surface oxidation of pure metals are too familiar to warrant discussion here.

Alloys, on the other hand, oxidize in a variety of ways, only vaguely understood, and thus give rise to a number of unanticipated effects. Perhaps the most commonly encountered of these is the alteration of the alloy composition. In the majority of cases the various elements in an alloy oxidize at different rates, which are not proportional to the concentration of the element in the alloy. Thus in extreme cases (which are not uncommon), the more reactive element may oxidize alone, leaving the less reactive element unattacked and changing the alloy composition in a layer

adjacent to the surface of the metal. The ancient process known as the "blanching" of silver depends upon the removal of copper from the surface of a silver-copper alloy; this is done simply by oxidizing the material at an elevated temperature in the air. An easily removed copper oxide scale is formed and the work is left with a surface layer of nearly pure silver. Gold alloys may be similarly enriched.

There are innumerable examples of inadvertent composition change accompanying surface oxidation where a scale is formed and also where no scale is formed. Iron-carbon and nickel-carbon alloys may lose carbon in the form of carbon monoxide or carbon dioxide in the course of surface oxidation; platinum-rhodium thermocouples may lose rhodium without the formation of any scale because the rhodium oxide evaporates as it forms.

Conversely, in other alloys early selective oxidation seems to halt the loss of alloying elements by forming a protective oxide scale which provides a barrier to further diffusion. Brasses heated in the absence of oxygen tend to lose zinc by volatilization. If heated in the air, however, a protective film of zinc oxide quickly forms and retards the further loss of zinc. This condition is to be associated with the defect in brass known as red stain, which appears in areas where oxidation has been restrained by a deposit of carbonaceous material or other obstruction that prevents the formation of the protective oxide layer; elsewhere the brass color is maintained by the protective action of the zinc oxide.

Subsurface Oxidation

Wherever the minor component of an alloy forms the more stable oxide, subsurface oxidation is possible. The modes of occurrence of such oxidation are almost as numerous as the alloys in which they are observed, but usually may be classified as one or a combination of the types: (1) general precipitation of separate parti-

cles of the oxide of the alloying element within a matrix of the major metal, (2) deposition of relatively thin layers of the oxide of the alloying element along the grain boundaries or special planes of the major metal or (3) envelopment of particles of the major component in a matrix of the oxide of the alloying element. In most cases oxidation proceeds by the inward diffusion of oxygen and the outward diffusion of the alloying element, the two meeting and reacting at an advancing interface below the outermost layer of metal. True subscale formation (precipitation of oxide within a metallic matrix) occurs chiefly in dilute alloys at high temperatures; grain-boundary oxidation occurs preferentially at lower temperatures (commonly at the temperatures of hot-working and heat-treatment) and in the more concentrated as well as in dilute alloys; continuous scales, containing embedded metal, appear most often among alloys containing large quantities of the oxidizing element.

The practical aspects of subsurface oxidation generally arise either from the presence of weakening films of oxide or from the depletion of the surface zones of the metal in the alloying element. Occasionally the depletion is found to extend entirely through the material.

Hensel, Larsen and Holt⁵ have described what they call a "birch-bark effect" in complex copper alloys that contain various quantities of cobalt, beryllium, silicon, cadmium and phosphorus, which are used for springs. When these alloys are heated in the air there appears a subscale which sometimes becomes detached when the springs are bent but sometimes remains firmly attached. In either case the subscale is harmful because the penetration is of the intercrystalline type and the notches so formed greatly reduce the fatigue life of the springs. It was found possible to prevent oxidation only by heating in hydrogen.

A somewhat similar effect was recently encountered when a manufacturer of Lake

copper sheet attempted to reduce the amount of pickling necessary after intermediate anneals by changing from a highly oxidizing to a nearly neutral atmosphere in the annealing furnace. The resultant sheet was brittle and was found to contain grain-boundary films, presumably of oxides of iron, arsenic or other impurities present in the copper. Evidently, in the earlier practice, surface oxidation had been more rapid than internal oxidation; thus all effects of oxidation were removed in pickling. Ductile copper was again produced by returning to this procedure. It should be noted that the use of a reducing anneal was avoided as a remedy in this case because of the danger of the hydrogen reduction embrittlement of this copper which is not oxygen free. Another manufacturer reports a parallel effect in the production of copper rod; if grain-boundary oxidation occurs, the material becomes difficult to form by cold drawing and breaks away in chips during knurling.

A number of troublesome occurrences of internal oxidation in ferrous materials have been reported. For example, Welchner and Roush⁶ within the current year demonstrated that certain NE steels containing residual silicon or aluminum form a grain-boundary subscale in the course of carburization. The carbon monoxide used in supplying carbon also provides oxygen. Casehardened gears made of these steels were found to have short life. Failures of stainless-steel electric heating elements have also been traced to intergranular oxidation, presumably of the chromium.

Among cases of similar damage to mechanical properties resulting from internal oxidation that have been mentioned in the present survey are: rough surface on cold-drawn copper-chromium alloys that had been annealed in the air; the failure of Nichrome in the presence of hot air or carbon monoxide; poor buffing qualities in alloys of silver containing copper, zinc, cadmium, magnesium or beryllium if

they have been annealed in the air and the oxides of these metals precipitated internally (in sterling silver the effect is most familiar and is known as "fire"); and the

heated to 980°C. in the air their age-hardenableity is destroyed.

The electrical properties of alloys, being very sensitive to composition, are also



FIG. 1.—SILVER-CLAD STEEL, SILVER AT THE TOP, COLD-ROLLED, ANNEALED 4 HOURS AT 870°C. IN AIR AND AIR-COOLED. UNETCHED: $\times 100$.
Iron oxide is visible at the interface and just within the silver layer.
(Courtesy J. L. Christie and C. H. Chatfield.)

deterioration of light metal castings (aluminum and magnesium) and certain wrought alloys during heat-treatment. In the last named, it is not certain that internal oxidation is involved. Stroup¹² has shown that the duralumin-type alloys lose strength and ductility if heat-treated in moist air.

Another group of effects of internal oxidation is to be associated with the withdrawal of an alloying element from solid solution. Age-hardening copper-beryllium alloys are particularly sensitive to internal oxidation because of the great reactivity of beryllium. If the solution heat-treatment of this material is carried out under oxidizing conditions the age-hardening characteristics may be destroyed in a surface layer, or, in the extreme, throughout the metal. A similar behavior is observed with chromium alloys; when

subject to modification by internal oxidation. It has long been recognized that the temperature coefficient of Manganin wire can be altered by heating in air. Likewise, base-metal thermocouples slowly change their electromotive force with time at temperature in the air, and this is thought to be the result of internal oxidation. Smart and Smith⁷ have shown that copper containing small quantities of several oxidizable elements, including antimony, cadmium and tin, suffers a rise in conductivity and a decrease in the recrystallization temperature when heated in the air.

Oxidation of Bi-metals

A special case of internal oxidation is found in the handling of certain bi-metal products. This is illustrated by the behavior of silver-clad steel when heated for

protracted intervals in air at temperatures as low as $425^{\circ}\text{C}.$; iron oxide forms near the junction of the two metals and the coating tends to spall. Oxygen, which diffuses through the silver coating, reacts with dissolved iron in a zone within the silver adjacent to the iron and also at the interface (see Fig. 1, presented through the courtesy of J. L. Christie and C. H. Chatfield, who have described the effect under discussion). A similar deterioration of silver electroplates on base metals has been known for some time and may be presumed to occur in the same way.

Reduction of Contained Oxides

Many commercial metals and alloys contain oxygen either in solid solution or in the form of an oxide. When such materials are heated in the presence of hydrogen, carbon monoxide or similar reducing gases, the hydrogen or carbon may diffuse into the metal and there reduce the oxides or react with the oxygen to form insoluble water vapor or one of the gaseous oxides of carbon. If this occurs where the products of reaction are confined, a considerable pressure may be generated and blisters or cracks will form.

Perhaps the best known occurrence of this type of action is that of the hydrogen embrittlement of tough-pitch copper. Heyn⁸ early analyzed the process and it is now known that in copper it is caused by hydrogen, and no other reducing gas, reacting with copper oxide, alloy oxides, or dissolved oxygen in the copper to form water vapor under pressure. Cupronickel alloys and oxygen-bearing iron are also subject to this kind of embrittlement (to be distinguished from the "hydrogen embrittlement" of iron by the presence of dissolved hydrogen in the absence of oxygen). It is interesting that, although Heyn⁹ described the reduction embrittlement of iron in one of the few attempts that have been made to interest the layman in the science of metals, the users of

iron have almost lost sight of the phenomenon, probably because most ferrous materials carry too little oxygen except that in the form of difficultly reduced oxides.

Despite general familiarity with the hydrogen embrittlement of copper and a thorough understanding of means of combatting it, the metallurgist continues to be plagued with unexpected occurrences of the effect. Two recently reported cases will serve to indicate the diversity of circumstances under which the damaging conditions may be met. Tough-pitch copper washers were being annealed in the course of their manufacture. To avoid excessive oxidation the treatment was conducted in a closed container and the washers were embedded in iron chips, to prevent sticking. Hydrogen embrittlement occurred and was traced to the presence of a small quantity of moisture and oil on the iron chips. It should be recalled that iron, releases hydrogen and it is possible that oil is similarly decomposed. The trouble was avoided by the use of a phosphorus-deoxidized copper.

In the second case, tough-pitch copper pipe was being brazed in an assembly; at the edge of the joint the copper was embrittled. Here hydrogen was present in the flame used for brazing. Again oxygen-free copper was substituted, although the difficulty might have been avoided by more careful control of the flame and by limiting the time during which the copper was heated. It is noteworthy that tough-pitch copper is currently being handled in bright-annealing (reducing) atmospheres by keeping the temperature as low as possible ($425^{\circ}\text{C}.$) and avoiding long heating times.

Another important result of the reduction of contained oxides is found in the blistering of galvanized iron. Just before the steel is dipped in zinc it is pickled to remove dirt and scale. In this step the iron

absorbs hydrogen. If oxides are present within the iron or on its surface, the hydrogen reacts to produce water vapor at the galvanizing temperature and a blister appears. The best remedy is to use clean steel. Another similar effect is encountered in the enameling of ingot iron. If the iron contains carbon it reacts with the oxides of the enamel during baking and produces blisters, known as "pop-pers." Ordinarily ingot iron contains insufficient carbon to cause blistering, but if the metal has been subjected to an anneal in the presence of carbonaceous gases it may absorb sufficient carbon to cause trouble.

When wires are sealed in electric light bulbs or vacuum tubes, damaging bubbles may form in the glass adjacent to the metal as a result of the reduction of oxides in the metal by reducing gases in the flame used to melt the glass. A typical example is found in nickel-manganese (4.5 per cent) wires that periodically gave trouble until special precautions were taken to maintain a neutral flame. Conversely, carbon in the wire may react with the oxides of the glass to produce carbon monoxide bubbles. Sometimes these difficulties are solved by using an oxygen-free alloy or by coating the wire with a material that hinders diffusion; copper-clad wires prevent gas evolution arising from the reaction of alloyed carbon with the oxides of the glass, because carbon does not diffuse through copper.

Occasionally such strongly reducing conditions are met that materials not ordinarily thought of as being subject to reduction effects are attacked. Thus in the manufacture of diphenyl, the refractory oxides commonly present in steel are reduced and steel pressure vessels develop leaks. Oxide-free materials give better life in this application.

Alternate Oxidation and Reduction

Related to the effect of reducing gases upon metals containing oxides is the effect

of subjecting metals alternately to oxidizing and reducing conditions. In the initial exposure the metal becomes charged with oxygen or a reducing agent. Upon subsequent exposure to the reverse condition a compound gas such as water vapor or carbon monoxide is formed within the metal. Again this gives rise to cracks, blisters and similar discontinuities.

The precious and semiprecious metals are notably sensitive to alternate oxidation and reduction. For example, a palladium-silver (60-40) alloy is commonly annealed in a reducing atmosphere. When the furnace is opened to withdraw or introduce a charge, some air may enter and come in contact with the metal, and blisters then form on the alloy. Pure palladium and pure silver behave in much the same way. Indeed, palladium has been known to form blisters at room temperature when stored in the air after first being charged with hydrogen by electrolysis. Martin and Parker¹⁰ have recently described the deterioration of silver both when reduction follows oxidation and when oxidation follows reduction. Copper behaves similarly but the damage to copper is less pronounced; tiny blowholes form but no large blisters or cracks.

Repeated cycles of oxidizing and reducing conditions promote the disintegration of materials that are not particularly sensitive to either condition alone. Apparently minute cracks, caused by grain-boundary oxidation and which would grow only slowly under constant oxidation, are freed of the obstructing filling of oxide during the reduction phases, and so admit gas more readily on subsequent oxidation. Thus Nichrome heating elements are found to deteriorate more rapidly in variable atmospheres; in a specific instance damage was found when operating at 955°C. The chromium oxidizes preferentially in this alloy, leaving a residue of metallic nickel. In the absence of severe damage of the kind just described, superficial embrittlement

may lead to a bad surface in metal that is subsequently cold drawn. A number of other nickel alloys are said to be subject to such surface effects.

Nitrogen

The solubility of stable nitrogen in the common solid metals is generally small; with the result that few technically important effects of dissolved nitrogen are recognized. Iron and iron alloys will absorb small quantities of nitrogen from the air and this contamination is effective in decreasing the rate of the austenite decomposition, especially in the nickel-chromium austenitic steels.¹¹ It is thought also that the absorption of nitrogen by sheet steel during annealing increases its tendency toward strain-aging. Nitrogen can be removed by a hydrogen treatment analogous to decarburization except that ammonia gas is formed.

Dissociated nitrogen, on the other hand, diffuses rapidly into iron at slightly elevated temperatures, produces unstable compounds with the iron and greatly increases its hardness. Ammonia (NH_3), or cyanides $\text{X}(\text{CN})$, are used to supply the atomic nitrogen. The dissociation pressure of the unstable compound Fe_4N has been shown by Emmett, Hendricks and Brunauer¹² to be of the order of 60,000 lb. per sq. in. at 420°C .; that is, the decomposing compound will build up this pressure of molecular nitrogen. For this reason nitrogen diffuses out of iron rapidly when the nitriding atmosphere (ammonia) is removed, leaving a surface film of nearly pure iron and subsurface layers of the nitrides.

In nitriding practice it is customary to use an iron-aluminum alloy (or calorized iron or steel). The aluminum nitride is relatively much more stable and forms in preference to iron nitride in a way quite analogous to the formation of oxide subscales. Such nitrided layers are stable. Occasionally nitriding of this kind is unintentional and is damaging to the material;

Kanthal furnace windings and other ferrous heating elements containing aluminum are subject to slow nitriding in the air and eventually become brittle in use.

Many of the less common metals absorb nitrogen in relatively large quantities and are generally made brittle by its presence. A notable example is chromium; among the others are such metals as tantalum, zirconium and related elements.

Sulphur

Sulphur is similar to oxygen in its interaction with metals. Usually it makes its appearance in furnace gases in the form of a compound such as SO_2 or H_2S and is known to dissolve in significant quantities in nickel, iron and copper. With nickel, sulphur forms a eutectic melting at 645°C ., well within the normal working range. Thus a liquid nickel-sulphur alloy is produced by the contact of nickel with sulphur during annealing. Diffusion proceeds most rapidly at grain boundaries where a liquid film appears as the penetration progresses. This causes the nickel to become hot short. Upon subsequent cooling a grain-boundary film of a brittle nickel-nickel sulphide eutectic remains, and this makes the metal cold short. Most nickel-rich alloys, including those used in thermocouples and electric heating elements (Nichrome), behave similarly except that additions of magnesium or manganese react preferentially with sulphur and make a small contamination tolerable. The best insurance against sulphur embrittlement is, of course, the elimination of sulphur gases. The sulphide eutectic with iron occurs at a higher temperature and embrittlement by this mechanism is less common therefore.

Sulphide scales, corresponding to oxide scales, are formed on copper and several other metals. Little is known about these and their possible influence upon the working properties of the metals.

Stroup¹³ has disclosed that some aluminum alloys are damaged by heat-treat-

ment in atmospheres containing sulphur dioxide. There is a large decrease in ductility and a smaller loss in strength, brought about by the development of a grain-boundary deposit of some reaction product. This difficulty is encountered when magnesium and aluminum alloys are heat-treated successively; sulphur dioxide is used in the furnace atmosphere to prevent the oxidation of magnesium.

Miscellaneous

Perhaps the most important deliberate application of gas-metal diffusion is in the production of coatings by cementation. The numerous processes are similar in their mechanisms. Usually the metal is bathed in a vapor of a hardening element, or one of its compounds, at an elevated temperature. The alloying element diffuses into the work and forms surface layers of intermetallic compounds if such are stable. Successive alloy layers correspond to the stable phases in the order in which they appear in the phase diagram, at the temperature of cementation, beginning with the pure metal on the inside and ending at the outside with the phase richest in the alloying element that is stable at the vapor pressure of the system. Upon subsequent cooling, phase changes that obscure this structural development often take place. Among the cementation treatments commonly employed are: carburizing, effected with CO or other carbonaceous gases; calorizing with aluminum, ferroaluminum or aluminum chloride; chromizing with chromium, ferrochrome or chromium chloride; ihrigizing with silicon, ferrosilicon and silicon carbide with or without chlorides; boronizing with boron powder or ferrobore; sherardizing with zinc or zinc salts, and stannizing with stannous chloride.

As might be expected, the cementation processes have their counterparts in unwanted contamination. For example, platinum thermocouples can be damaged

by absorbing silicon. This can happen in the presence of hydrogen, where it is presumed that silicon hydride forms a carrier vapor. Zinc present in a furnace atmosphere is destructive to Nichrome heating elements. Brass or galvanized iron will serve to provide the zinc vapor.

CLOSURE

Many more examples of the working of gas-metal diffusion in industrial processes will occur to the reader, no doubt. The literature, which has not been reviewed here, except incidentally, contains many volumes on this subject. Yet, considering the demonstrated technical importance of gas-metal diffusion, this knowledge is wholly inadequate. On the theoretical side, too little is known of the mechanisms connecting diffusion with the physical results that are observed. On the practical side too little attention has been paid to the accumulation of the data that would permit the utilization of such theory as exists. There need be little doubt that future industrial developments will call for a greater understanding of gas-metal behavior. The trend is emphasized by the rapid increase in the use of controlled atmospheres in the past decade.

ACKNOWLEDGMENTS

The author wishes to express his deep gratitude to the many specialists who have taken the time to contribute suggestions and experiences for this compilation despite the pressure of their duties. It has been thought best not to acknowledge the sources of information in the text, partly because almost every subject was mentioned by a number of correspondents and partly because of the danger of misquoting an individual where stories from different sources have been combined. None of the correspondents has had an opportunity to review the manuscript and any misstatement should be regarded

as the fault of the writer. Very special thanks are due to: R. S. Archer, W. Blum, H. L. Burghoff, F. E. Carter, C. H. Chatfield, J. L. Christie, B. Egeberg, O. W. Ellis, E. W. Engle, K. L. Fetters, E. F. Fischer, B. W. Gonser, J. D. Hanawalt, M. F. Hawkes, F. R. Hensel, C. W. Herty, Jr., A. J. Herzig, S. L. Hoyt, M. A. Hunter, J. Johnston, L. W. Kempf, A. B. Kinzel, R. P. Koehring, W. Lynes, G. K. Manning, C. L. Mantell, D. L. Martin, R. F. Mehl, A. J. Phillips, N. B. Pilling, W. B. Price, C. H. Samans, E. E. Schumacher, C. S. Smith, S. Tour, E. M. Wise and R. T. Wood.

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DISCUSSION

G. P. HALLIWELL,* Chicago, Ill.—I have not had an opportunity to read this paper; my first acquaintance with it was during Dr. Rhines' presentation. I gathered from the forepart of the paper that all the difficulties in gassed or porous metal are caused by gases in solution in the metal per se. It happens that I am associated with a branch of the metal industry that casts metal in sand. I want to add a word of caution to any foundrymen in this audience or to any who may read this paper later; that is, do not ascribe all the troubles in the foundry to gas in the ingot before it is melted. Anyone casting metal in sand will realize that this is not true. We admit that it does happen sometimes, but gassed metal may be caused by the conditions of melting, and porous metal may be a result of the use of the wrong type of sand—too old or too green a sand; sand with too low a permeability or too high a moisture content; or sand that is improperly rammed. Porosity may also come from cores made from the wrong type of sand, or cores that are improperly vented or insufficiently baked. If all these conditions are corrected—assuming, of course, that the metal is satisfactory in the beginning—the opportunities for obtaining gassed or porous castings are reduced to a minimum.

I am very much interested in Dr. Rhines' note that thunderstorms might have an effect. Some people may smile at it, but I have noticed repeatedly that when there is a spell of humid weather, more porous castings are made than during a dry spell. This is not necessarily because we may or may not have used metal that has been stored for some time and accumulated a film of moisture. During periods of high humidity, we have experienced some heats that are more prone than others to produce porous castings. It is difficult to say whether this is due to the absorption of hydrogen from the decomposition of the water vapor or to some other undetermined factor. It is possible that there is something to the question of humidity, and the accompanying association with a thunderstorm that Dr. Rhines mentions.

SAM TOUR,† New York, N. Y.—I want to compliment Dr. Rhines on a very excellent

* Director of Research, H. Kramer and Co.

† Sam Tour and Co., Inc.

compilation and a very excellent paper. I think he has done a remarkable job, but I do not want to let Mr. Halliwell's discussion go without some rebuttal.

It is not true that the metal is never at fault. Let us not give the metal a clean bill of health quite so easily. Enormous quantities of metals produced and sold contain gases. A particular foundry that has used a particular metal repeatedly and for a long time, producing good castings, has adjusted its practice to accommodate the amount of gas in the metal by melting a little more oxidizing, for example. If that particular foundry should receive a shipment of metal that did not have the gas in it, the foundry would have trouble. Vice versa, if foundries that are operating continuously and satisfactorily with metal that does not have gas in it receive a metal that has a little gas in it, great difficulties arise.

Gas is not always a bad actor—it is a bad actor when it is in the wrong place. We should not say that all remelted metal is gas-free, because we know many castings that are not gas-free and that give trouble. It is perfectly possible to have ingot metal that is gassed. In fact, it is not uncommon to see bulged ingots in the form of ingot metal.

Foundrymen should not be told to look first to sand or something else. They should look at the whole picture and determine what practices or what raw materials have been changed.

I should like to add some comments on the effect of thunderstorms. There are numerous things in a foundry that affect the gas-metal situation other than the metal itself or melting. The weather can affect these other things even more rapidly than it affects the metal. It is quite common to have trouble during a thunderstorm in melting certain metals that

are readily gassed, such as manganese bronze. However, a study of the particular foundry having trouble often shows that a lot of charcoal is being used, or trick nostrums in the form of fluxes identified by trick numbers and compositions unknown. Fluxes of this type usually contain hygroscopic salts. When humid weather comes along, and gassy metal is produced, the blame should not be placed on the metal or on moisture in the air going to the burner where fuel is burned to moisture. The trouble may be from moisture in the charcoal, the trick fluxes, the salt, the ladle linings, or other materials used in the foundry. Gases in metal can come from numerous sources.

F. N. RHINES (author's reply).—In general, the observations of Messrs. Halliwell and Tour are in accord with the impressions that I have held and have attempted to set forth in the paper.

Mr. Tour has relieved me of the necessity of responding to the question of gassed ingot and has done so far more capably than I could have done. There remains for discussion, however, the matter of the influence of the condition of the sand upon porosity. In this connection a clear distinction should be drawn between "surface blows" caused by gas pressure from without and porosity caused by the release of gas by the metal at the time of freezing. To the best of my knowledge, good experimental evidence of the gassing of metal by wet sand in the mold, or of the contrary, is lacking; it would be surprising to me, however, if any metal could absorb enough gas in the few moments that it remains liquid in contact with the sand to materially influence its freezing characteristics.

The Degassing of Metals

By F. J. NORTON* AND A. L. MARSHALL*

(Chicago Meeting, October 1943)

THE object of this investigation was to make a comprehensive study of the degassing of molybdenum in order to determine how rigorous a treatment was necessary to completely remove sorbed gases from molybdenum electrodes in vacuum tubes. Some work has also been done with tungsten, nickel, iron and carbon. As a logical development of this work it has been shown that the gas is present throughout the body of the metal and a study has been made of the solubility of nitrogen in molybdenum and tungsten and the rate of diffusion of nitrogen through molybdenum has been calculated.

Tests were made on molybdenum from all the commercial sources and no difference was discovered in the nature of the gases present, the amounts or the ease of removal. The reason for this was apparent when a study was made of the manner in which gases are absorbed by gas-free molybdenum. It is necessary to heat molybdenum to 1760°C. in a vacuum of the order of 0.001 micron for a time which varies linearly with the thickness, in order to obtain a condition in which no further gas is evolved by the sample. A sample so degassed can be handled and subsequently assembled in a tube and then degassed readily. The gases obtained from molybdenum are carbon monoxide and

nitrogen, the nitrogen being the more difficult to remove.

APPARATUS AND TECHNIQUE

The apparatus is shown in Figs. 1 and 2. It consisted of two units, a degassing system and an analytical system. Each had a bake-out oven, as shown surrounding the systems in the sketches. The system will be traced, starting from the sample in the degassing system.

A water-cooled quartz chamber surrounded the sample. The high-frequency coil, which heated the sample, extended only around this chamber and was cooled by an air blast. High-frequency power of 1800-meter wave length was obtained from a self-rectifying oscillator circuit with a maximum power input of 20 kw. A graded seal connected the quartz to the rest of the apparatus, which was of hard glass. The temperature of the molybdenum sample was observed by an optical pyrometer through an optical window about 40 cm. distant from the sample. Since the object viewed under these conditions was not a black body, true temperature was not observed, but the so-called "brightness temperature." The correction of this to true temperature is discussed in a later section.

The apparatus was taken apart just above the graded seal; the quartz chamber was slipped off, washed with nitric acid, water and alcohol, and dried by an air stream. The old sample was removed by unscrewing the lower nut, and the new

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*General Electric Co., Schenectady, N. Y.

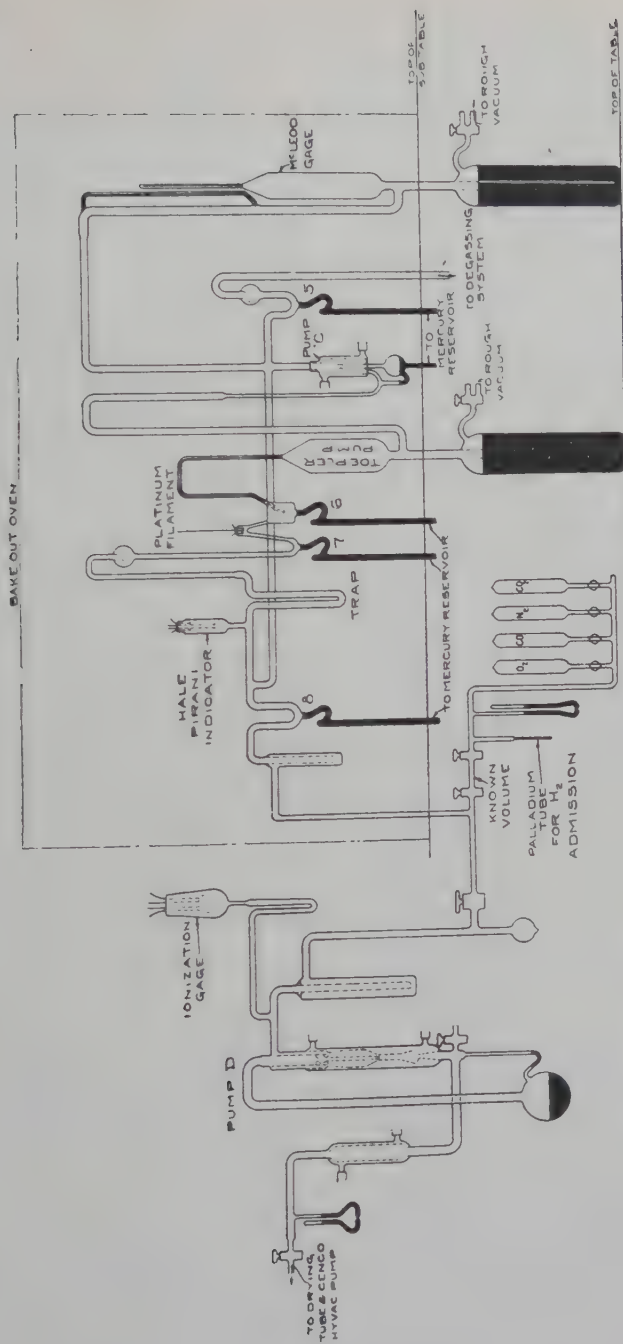


FIG. 2.—ANALYTICAL SYSTEM.

one was put on. Great care was taken not to handle any of the metal parts.

The apparatus was then sealed together again and evacuated by pump *B*. The mercury in the various traps was let down below the level of the bake-out oven. It was essential to attain a good vacuum before applying heat; otherwise the sample would become badly oxidized. Liquid air was put on the ionization gauge trap. A small tube furnace extended over the quartz bulb, and a large bake-out oven extended over this and the whole system. The quartz was baked out at 800°C., reaching this during the last half hour of bake-out. The whole system was baked out at 450° to 470°C. for 1 hr. After cooling, the mercury was let up into pump *A* and traps 2 and 3 were closed. Cooling water was let into the pump *A*, trap and quartz jacket, and the pump started. At this point, the ionization gauge showed a vacuum of better than 0.001 micron. Previous work had also shown that with this design and bake-out procedure no liquid air was needed on the large trap. This enabled the condensable gases CO₂ and H₂O to be determined, though the determination of H₂O would have been problematical because of the avidity with which it is absorbed by baked-out glass. The water-cooled trap kept the mercury pressure low enough in the quartz chamber so that no glow discharge in mercury vapor occurred during heating of sample with high frequency.

The preceding bake-out gave conditions such that less than 0.02 cu. mm. of gas was collected with shutoff 4 closed and pump *A* running, over a period of 10 to 15 min. This has been found to hold even when the sample and quartz were at 800°C. Consequently, it is evident that the gases later evolved could come only from the sample. A poor bake-out was indicated by a slow, continuous evolution of gas. The test of collecting less than 0.02 cu. mm. of gas as measured

by the McLeod gauge was applied before every run.

DETAILED MANIPULATION

On making a run, shutoffs 4, 3 and 2 were closed, and with pump *A* running, high-frequency heating was applied to the sample. As the gas was given off and collected back of pump *A*, the pressure was measured on the McLeod and the Hale Pirani gauges. The latter was arranged as shown, so that the compensator was under a constant good vacuum.

When gas evolution apparently had ceased, the high frequency was shut off and pump *C* in the analytical system was started. This whole system had previously been baked out and evacuated, the large glass stopcock between the systems being open in the process. Shutoffs 8, 7 and 6 were closed, and when shutoff 3 was opened the gas sample was drawn over into the analytical system. The Toepler pump was operated during this time to reduce the back-up pressure of pump *C*.

After the sample of gas had been transferred, shutoff 3 was again closed and with a low pressure in the collecting end of the degassing system (0.01 to 0.03 microns) the high frequency was started again, to be sure that no more gas was being given off. The procedure was used because of the greater precision of the McLeod in the lower pressure ranges, for small quantities of gas.

The glass stopcock between the systems was then closed, as was shutoff 5, isolating the two systems. The degassing system was then available for another run. The sample of gas was in contact with mercury and baked-out glass only, except for the brief passage through the glass stopcock during its transfer, which reduces to a minimum the possibility of contamination.

The volume of the collecting part of the degassing system was determined by admitting dried nitrogen to the system with pump *A* operating. The volume of the

McLeod gauge was known from its calibration. Mercury was let into the gauge, trapping off a known volume of gas at a measured pressure; the rest of the collecting system was evacuated, shutoff 4 closed again, the nitrogen in the gauge admitted to the system and the pressure again measured. The ratio of the two pressures times the volume of the gauge gives the volume of the collecting system.

ANALYTICAL TECHNIQUE

The method was essentially that of Langmuir¹ for the analysis of small amounts of gases.

As described above, the sample was transferred to the analytical system, pump C was cooled and shutoffs 6 and 7 were opened. The sample then occupied the whole of the analytical system between shutoffs 5 and 8.

Liquid air was first applied to the trap and the decrease in pressure measured the CO₂ present in the sample. After this was measured, the gas sample was compressed again into the ignition bulb between 6 and 7. Pure oxygen of known amount was admitted to the system through shutoff 8 with liquid air on the trap. The gas sample was released into the system and the new pressure read after equilibrium was attained.

The sample and oxygen were compressed into the ignition bulb containing a 5-mil filament of pure platinum. This was heated to a dull red for 10 min. Previous work with known amounts of H₂, CO and O₂, in the analytical system, had shown that this time sufficed for the reaction of



The oxidation of hydrogen to water was very rapid at this temperature.

At first it was feared that in compressing samples containing oxygen with the small mercury pump, some of the oxygen might

react with the mercury vapor and the attendant decrease in pressure give a false indication. This point was tested by circulating pure oxygen, and also various combustible mixtures for $\frac{1}{2}$ hr., with the pump. No change in pressure was found. This is in conflict with the findings of Hibben² who dropped mercury through oxygen at low pressures and observed a decrease in pressure.

The sample of unknown gas, after undergoing combustion, was released into the system with CO₂ snow-ether on the trap. The decrease in pressure, if any, was due to the hydrogen and oxygen which had reacted, plus the oxygen which had combined with carbon monoxide. The contraction which followed when the liquid air was placed on the trap measured the carbon dioxide present. When the amount of carbon dioxide originally found was subtracted, the rest of the contraction represented carbon monoxide originally present, which was oxidized to carbon dioxide. The amounts of gas accounted for by this procedure were then subtracted from the original volume of sample, and the residual considered to be nitrogen. Preliminary work had shown that no oxygen was present in the gases from molybdenum.

Hydrogen was not a common constituent. Large quantities of hydrogen were collected when the bake-out was known to be poor, due probably to water vapor from the glass surfaces reacting with the hot molybdenum. There was also a possibility that some hydrogen came from the sample during the 800° bake-out.

TEMPERATURE MEASUREMENT

Temperature measurement was made by means of a Leeds and Northrup optical pyrometer of the disappearing-filament type. It was calibrated against a standard ribbon filament lamp. The emissivity has been given by Worthing^{3,4} as 0.352 at 2000°K., but the emissivity of our etched sample was

¹ References are at the end of the paper.

0.40. Thus our sample at a true temperature of 1760°C. had a brightness temperature of 1600°C.

The standard temperature used in most of the experiments, 1760°C. (1600°C.

center, and were from 20 to 250 mils (0.020 to 0.250 in.) thick, most of them being about 70 mils thick. There was a hole in the ring by which it was attached to a 100-mil molybdenum rod. This rod was

TABLE I.—*Gas Evolved from Molybdenum in Stages and at Single Temperatures*

Brightness Temperature, Deg. C.	True Tem- perature, Deg. C.	Gas (NTP), Cu. Mm. per Gram Sample	Gas Composition, Per Cent				Amounts of Gas, Cu. Mm. (NTP) per Gram Sample			
			N ₂	CO	CO ₂	H ₂	N ₂	CO	CO ₂	H ₂
EXPERIMENT 2. GAS IN STAGES FROM 70-MIL, 4.9-GRAM SAMPLE, CAUSTIC-DIPPED										
740	790	0.81	4	75	21		0.03	0.61	0.17	
940	1010	0.33	16	42	15	27	0.05	0.14	0.05	0.09
1120	1210	1.98	81	15		4	1.60	0.30		0.08
1312	1440	1.06	76	10	6	8	0.82	0.10	0.06	0.08
1600	1760	0.23	45	24	7	24	0.11	0.05	0.02	0.05
Total.....		4.41 wtd. } ave. }	59	27	7	7	2.61	1.20	0.30	0.30

EXPERIMENT 296. GAS AT SINGLE TEMPERATURE FROM 70-MIL, 4.9-GRAM SAMPLE, CAUSTIC-DIPPED

1600	1760	5.05	58	30	6	6	2.95	1.50	0.30	0.30
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EXPERIMENT 12 (FIG. 3). GAS IN STAGES FROM 72-MIL, 5.3-GRAM SAMPLE, CAUSTIC-DIPPED

740	790	1.03	5	66	20	9	0.05	0.68	0.21	0.09
978	1050	0.69	66	30	4		0.45	0.21	0.03	
1115	1210	1.70	95	5			1.61	0.09		
1320	1450	1.78	90	10			1.60	0.18		
1500	1650	0.22	90	10			0.20	0.02		
1600	1760	0.04					0.04			
Total.....		5.46 wtd. } ave. }	73	21	4	2	3.95	1.18	0.24	0.09

EXPERIMENT 34. GAS AT SINGLE TEMPERATURE FROM 72-MIL, 5.3-GRAM SAMPLE, CAUSTIC-DIPPED

1600	1760	3.8	94		6		3.5		.3	
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brightness temperature), was chosen because below it completion of gas evolution was too slow to be convenient, and above this temperature appreciable evaporation of molybdenum took place. This resulted in a clean-up of some of the gas given off, and it was found that runs at 100° above the chosen temperature gave less gas.

PREPARATION OF SAMPLE

The samples made from sheet molybdenum were in the form of rings $\frac{7}{8}$ -in. outside diameter with a $\frac{1}{16}$ -in. hole in the

threaded at one end and two molybdenum nuts held the sample in position. It was necessary to file three longitudinal grooves in the threaded end of the rod to prevent the nuts from sticking after the high-frequency heating.

The sheet molybdenum was cut with a hacksaw into rough shape. A $\frac{3}{16}$ -in. hole was drilled in the center, and a hole for the 100-mil wire for support of the sample. The outside was then turned off on a lathe, so a ring resulted, with the oxide, if originally present, on the faces.

The sample, on a clean molybdenum rod, was dipped into a bath of molten caustic with about 3 per cent nitrite in it at 450°C. About 30 sec. cleaned off the

successively higher temperatures and the gas evolved at each stage is collected and analyzed.

In these experiments the high tempera-

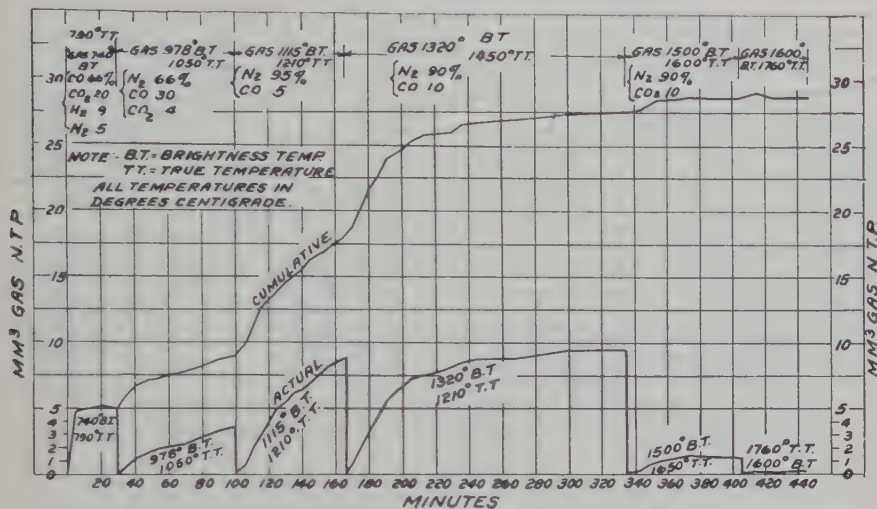


FIG. 3. —Gas evolved from molybdenum. 72-mil. 5.3-gram sample, caustic-dipped.

oxide. The ring was then dipped successively into hot water, 10 per cent hydrochloric acid solution, cold water, washed thoroughly in distilled water, dipped into grain alcohol and dried in a stream of air. Care was taken to avoid touching the sample at any stage of cleaning. It was handled with tweezers and kept wrapped in condenser paper.

Some samples, as noted, were further treated by electrolyzing in concentrated sulphuric acid, with a strip of molybdenum sheet as cathode and the sample as anode. The appearance of the electrolyzed samples was bright and shiny, compared to the dull gray of the caustic-dipped samples. The caustic-dipped samples showed clearly the fibrous structure of the metal.

NATURE OF GAS EVOLVED AT VARIOUS TEMPERATURES

Table 1 and Figs. 3 and 4 show the results obtained as a sample is heated to

temperature (800° to 1000°C.) bake-out oven was not put on the quartz. It received the 450° bake-out with the rest of the system. When the evolution of gas from the sample was at an end, or at a steady rate, for a given temperature, the sample was pumped over to the analytical system, and the rate checked again at low pressures in the collection system, to be sure of the rate, or of the complete cessation of gas evolution.

These experiments and the data summarized in Fig. 4 are of especial interest in showing the relative ease with which the constituent gases come off.

Hydrogen comes off most readily, at the lower temperatures, as Alleman and Darlington⁵ found with ferrous alloys. The amount of this is relatively small.

The next gas to appear in quantity is carbon monoxide, which comes off readily at 1000° and lower. It persists, in small amounts, to the higher temperatures.

Nitrogen is more difficult to remove and requires a temperature of 1200° and up

before it comes off. It is of interest to note that* molybdenum nitride may exist as shown by Langmuir.⁶

temperatures the time for complete degassing was excessive and at higher temperatures evaporating molybdenum cleaned

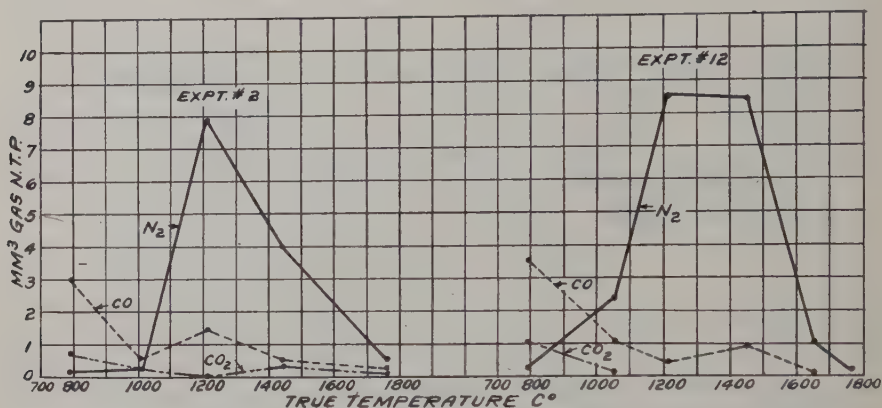


FIG. 4.—AMOUNT OF GASES GIVEN OFF AT VARIOUS TEMPERATURES. Molybdenum ring, $\frac{1}{16}$ -in. inside diameter, $\frac{1}{8}$ -in. outside diameter and 0.07 in. thick.

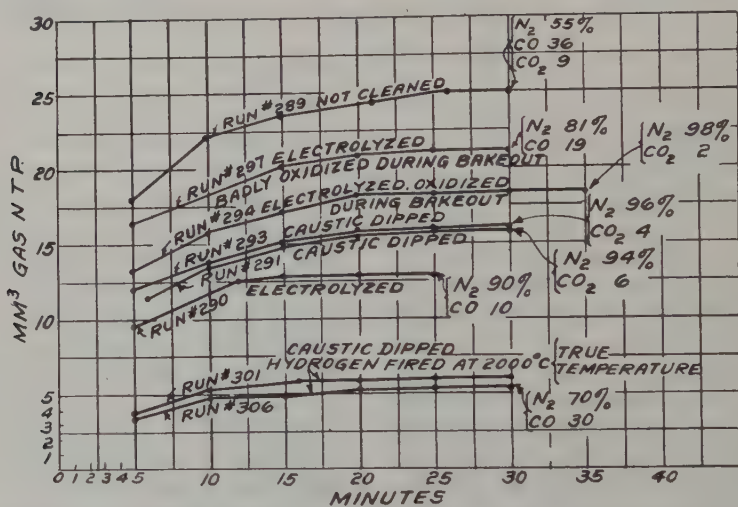


FIG. 5.—GAS EVOLVED FROM MOLYBDENUM. 70-MIL 5.1-GRAM SAMPLE DEGASSED AT 1760°C. TRUE TEMPERATURE.

EFFECT OF TREATMENT AND SOURCE ON GASES FROM MOLYBDENUM

In the light of the previous experiments it was decided to carry out all subsequent experiments at 1760°C. This seemed to be the optimum temperature; at lower

up some of the gas evolved. Samples degassed completely at 1760°C. gave off no further gas on being taken to higher temperatures.

Table 2 gives the total amounts and composition of the gases obtained from the samples of molybdenum from various

sources. Figs. 5 and 6 illustrate the rate at which the gases are evolved and together with the tables present the results obtained. From these data it is evident that samples

ent methods of manufacture, such as amount of working, and the gas content.

The rate of gas evolution was found to be of the first order and this together with

TABLE 2. —Molybdenum Samples Degassed at a Single Temperature

Stock No.	Expt. No.	Cleaning			Thick-ness, Mils	Time for Degas-ing, Min.	Gas Composition, Per Cent				Weight of Sample, Grams	Amount of Gas, Cu. Mm. (NTP) per Grain Sample				
		NaOH Dip	Elec-tro-lyzed	Hy-dro-gen-fired			N ₂	CO	CO ₂	H ₂		N ₂	CO	CO ₂	H ₂	Total
1760°C. TUBE TEMPERATURE																
3	268	*	*		73	25	88	12			5.1	1.8	0.25			2.05
3	272	*	*		73	25					5.1					2.1
3	271	*	*		73	22	93	7			5.1	1.5	0.11			1.61
4	286	*	*		70	25	95		5	2	5.0	4.5		0.24		4.74
4	287	*	*		70	25	86	12			5.0	3.5	0.5	0.08		4.08
4	288	*	*	*	70	25					5.0					1.2
4	300	*	*	*	70	20	81	16	3		5.0	0.86	0.17	0.04		1.07
4	305	*	*	*	70	25	91	9			5.0	0.88	0.09			0.97
5	296	*	*		70	15	58	30	6	6	4.9	2.9	1.5	0.3	0.3	5.0
5	309	*	*		70	20					4.9					2.8
7	27	*	†		250	115	63	27	5	5	17.9	1.13	0.48	0.09	0.09	1.79
8	31	*	†		250	120	95		5	11	17.9	0.95		0.05		1.0
10	263 ^a		*		70	70	35	65			5.1	2.7	5.1			7.8
10	274 ^b		*		70	20	82	15	3		5.1	3.1	0.6	0.1		3.8
10	302	*	*	*	70	40	59	36	5		5.1	0.71	0.43	0.05		1.19
10	304	*	*	*	70	16					5.1					0.86
11	276	*	*		25	11	78	19	3		1.8	6.4	1.6	0.2		8.2
12	307	*	*		69	30	68	26	6		5.1	3.4	1.3	0.3		5.0
12	308	*	*		69	20	95	5			5.1	4.0	0.2			4.2
1	299	*	*		25	5	81		2	17	1.8	6.5		0.2	1.3	8.0
1	298	*	*		25	4	85	4	3	8	1.8	6.2	0.3	0.2	0.6	7.3
2	289 ^c		*		70	26	55	36	9		5.1	2.7	1.8		0.4	4.9
2	297 ^d		*		70	25	81	19			5.1	3.4	0.8			4.2
2	294 ^e		*		70	30	98		2		5.1	3.5		0.1		3.6
2	290 ^f		*		70	15	90	10	4		5.1	2.3	0.3			2.6
2	293	*	*		70	25	96				5.1	3.0		0.1		3.1
2	291	*	*	*	70	25	94		6		5.1	2.9		0.2		3.1
2	301	*	*	*	70	25					5.1					1.2
2	306	*	*	*	70	25	70	30			5.1	0.7	0.3			1.0
9	285 ^g		*		69	2	22	76	2		5	1.8	6.1	0.1		8.0
9	279	*	*		69	30	75	22	3		5	2.8	0.8	0.1		3.7
9	292	*	*	*	69	20	95		5	8	5	1.6		0.1		1.7
9	284	*	*	*	69	45	63	29			5	1.0	0.4	0.1		1.5

* Piled clean; washed with benzol.

^b Oxidized during bake.

^c Not cleaned. No oxide on sample.

^d Badly oxidized in bake.

^e Oxidized in bake.

^f Not oxidized.

^g Handled after degassing, then not cleaned.

* Indicates that these received treatment of column heading.

† Unworked.

‡ Worked.

from all the different sources give about the same amount of gas and require about the same time for complete degassing. No correlation could be found between differ-

evidence presented later seems to show that the controlling factor in the gas evolution is the diffusion of gas to the surface from within the sample.

EFFECT OF VARIOUS METHODS OF
CLEANING

From the tabulations it is evident that methods of preparing the sample give

The decreasing amounts of carbon monoxide in the series in Table 3 is interpreted as more complete removal of surface grease and dirt, but from the curves in

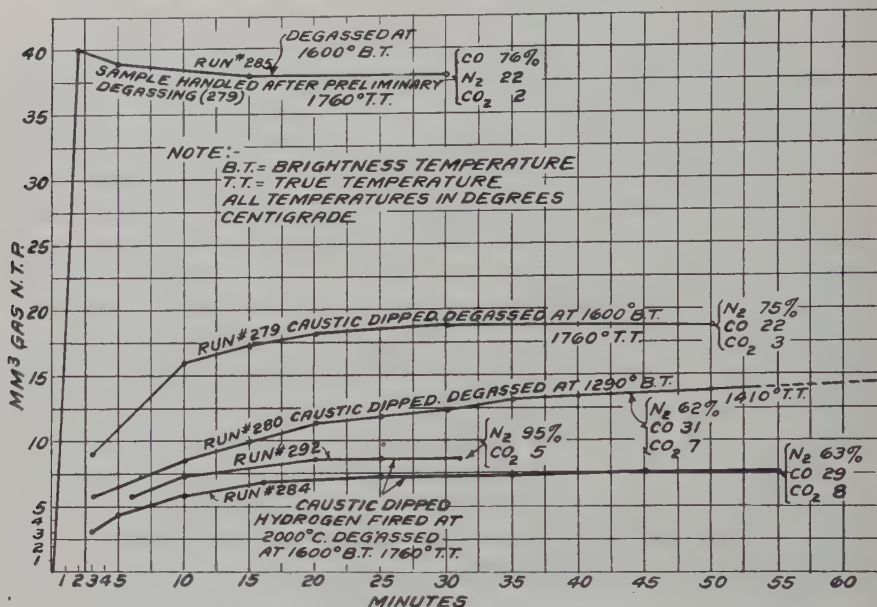


FIG. 6.—GAS EVOLVED FROM MOLYBDENUM. 69-MIL, 5-GRAM SAMPLE.

greater differences than appear in samples from various sources. A summary of the effect of various methods of cleaning on gas evolution is given in Table 3, in order of increasing effectiveness. The samples were all 70 mils thick. The first treatment represents the result of one experiment; the others are the average of several.

TABLE 3.—Effect of Method of Cleaning on Gases Evolved

Treatment	Time of Degassing, Min.	Amount of Gas, Cu. Mm. (NTP) per Gram Sample	Gas Composition, Per Cent		
			N ₂	CO	CO ₂
Filed clean and washed in benzol.	70	7.8	35	65	
Caustic-dipped.....	24	4.4	79.0	16.5	4.5
Electrolyzed conc. H ₂ SO ₄	20	3.3	88.5	10.5	1.0

Figs. 3 and 4 it is apparent that carbon monoxide continues to come out even at later stages of the degassing, apparently from the body of the metal.

The effect of dirt and grease is shown by experiments 285 and 279 (Table 2 and Fig. 6). A caustic-dipped sample was run in the regular manner, No. 279. It gave off 3.7 cu. mm. gas (NTP) per gram sample, 75 per cent N₂ and 22 per cent CO, and required 30 min. for complete degassing. This same sample was taken out and handled, then put back into the system and a regular bake-out given. Then on degassing (experiment 285) at 1760°C., 8.0 cu. mm. gas NTP per gram sample came off in 2 min. It consisted of nitrogen 22 per cent, carbon monoxide 76 per cent. The rapidity with which this gas comes off can be explained by the fact that it is absorbed only on the surface of the sample.

PERMANENCE OF DEGASSING

One of the most striking things found in this investigation of molybdenum was that a sample once degassed stays degassed, if proper precautions are taken. The most important requirement is to avoid handling the sample, as shown in the preceding section.

If precautions are taken, and the sample handled with tweezers and kept wrapped in condenser paper, the surface contamination is reduced to a minimum, as in experiment 104. A sample was degassed in the Arsem furnace,* then in the quartz apparatus. It was taken out, handled only with tweezers and kept wrapped in $\frac{1}{2}$ mil condenser paper for 42 days. On degassing this sample in the regular manner after that length of time, the results shown in Table 4 were obtained.

TABLE 4.—*Experiment No. 104, Sample 70 Mils Thick*

Gas Evolved, Cu. Mm. (NTP) per Gram Sample	True Temp., Deg. C.	Time for Complete Degassing, Min.	Gas Composition, Per Cent		
			N ₂	CO	CO ₂
0.28	1275	10	15	73	12
0.10	1760	10	31	50	19
Total 0.38					

Similar results were obtained for a sample which had been degassed, taken out, caustic-dipped, washed in water and alcohol, and degassed again. This sample weighed 4.9415 grams before caustic dip, 4.8900 grams after caustic dip; i.e., 0.0515 loss on NaOH dipping, or 1.04 per cent loss. The original sample was 72 mils thick; the edge area makes up 24 per cent of the total surface area. Hence the caustic dip, assuming uniform attack, reduced the 72 mils thickness by $0.76 \times 0.0104 \times 72 = 0.58$ mils. The removal of this thickness of molybdenum had the result shown in

* An Arsem furnace is a vacuum furnace heated by a carbon resistor.

Table 5 on the amount of gas at the second degassing. This indicates that the gas has been removed at least to a depth of 0.58 mils. The question of the depth to which degassing has proceeded is discussed in the following section.

TABLE 5.—*Experiment No. 24*

Gas Evolved, Cu. Mm. (NTP) per Gram Sample	True Temp., Deg. C.	Time for Degassing, Min.	Gas Composition, Per Cent	
			N ₂	CO
0.27	1760	3	87	13

TABLE 6.—*Experiments on Samples Exposed to Wet Air and Degassed a Second Time**

Experiment No.	Gas Evolved, Cu. Mm. (NTP) per Gram Sample	Gas Evolved, Cu. Mm. (NTP) (Total)	True Temp. Deg. C.	Time for Complete Degassing, Min.
103.....	0.01	0.07	1060	5
	0.05	0.24	1760	5
	0.06	0.31		
110.....	0.03	0.15	1260	5
	0.02	0.10	1760	5
	0.05	0.25		

* Regular bake-out procedure, glass at 450°C. quartz and sample at 800°C.

Two other experiments may be cited in which the samples were not taken from the apparatus, but exposed to wet air after degassing and then degassed the second time. Small amounts of gas were obtained, corresponding closely to a monomolecular layer. The sample of experiment 103 had stood in contact with the atmosphere for 15 hr., experiment 110 for 40 hr. The 0.25 cu. mm. of gas from experiment 110 was 57 per cent N₂, 43 per cent CO. This, incidentally, represents the smallest amount of gas that was analyzed.

In Langmuir's paper on the absorption of gases by glass, mica and platinum,

TABLE 7.—*Arsem Furnace Experiments*
Molybdenum Samples 0.070 in. Thick

Experiment No.	Furnace Conditions				Degassing		Gas Composition, Per Cent			Amount of Gas, Cu. Mm. (NTP) per Gram Sample
	Time of Firing, Hr.	Temperature, Deg. C.	Vacuum		Temperature, Deg. C.	Time for Complete Degassing, Min.	N ₂	CO	CO ₂	
			McLeod, Microns	Hale-Pirani, Microns						
39	1	1625	125	100	1760	15	58	37	5	1.13
40	2	1625	50	80	1760	15	66	34		0.72
65	1	1780	100	100	1760	20	50	43	7	1.75
66	1½	1780	150	100	1760	15	71	24	5	0.71
70	1	1770	75	100	1760	5	10	84	6	0.58 ^a
77	2	1780	50	90	1760	10		90	10	0.83
									Ave.	0.95

^a Best.TABLE 8.—*Tungsten Furnace Experiments*
Molybdenum Samples 0.070 in. Thick

Experiment No.	Furnace Conditions					Quartz Apparatus Degassing					
	Time of Degassing, Hr.	Temperature, Deg. C.	Vacuum			Temperature, Deg. C.	Time for Complete Degassing, Min.	Gas Composition, Per Cent			Amount of Gas, Cu. Mm. (NTP) per Gram Sample
			McLeod, μ	Hale-Pirani, μ	Ionization Gauge (Liquid Air On), μ			N ₂	CO	CO ₂	
75	1	1800		10	1.5	1760	20				1.26
76	1½	1800	1.5	10		1760	5	15	74	11	0.54
79	1	1800		5	0.4	1150	5	3	88	9	0.47
						1760	15	13	76	11	0.33
											0.80 ^a
96	1	1800	3	8	0.8	1760	40	17	79	4	1.57
97	1½	1800	2.5	6	0.6	1250	10		63	37	0.22
						1760	30		85	15	0.40
											0.62
99	2	1800	1.5	4	0.3	1300	5	23	65	12	0.13
						1760	15		72	18	0.31
											0.44 ^a
120	1½	1950	2	8		1280	20	60	40		0.18
	10	1650	1.4	5		1760	25	70	30		0.31
											0.49
125	1	1950	2	6		1300	20	21	67	12	0.29
						1760	20	30	59	11	0.49
										Ave.	0.78
											0.82

^a Best.

he shows that for an average molecular diameter of 3×10^{-8} cm., a monomolecular layer over 1 sq. cm. of surface corresponds to 0.04 cu. mm. gas (NTP). The samples of molybdenum used in this investigation had a total surface area, (from the gross dimension) of 7.65 sq. cm. which should give 0.306 cu. mm. of gas for a monomolecular layer. This agrees with the values found above of 0.25 and 0.31 cu. mm. within the limits of accuracy for the method.

A number of experiments were made to determine whether a high vacuum was necessary to degas molybdenum. Samples were heated in a carbon tube vacuum furnace, a tungsten tube vacuum furnace and in hydrogen of various degrees of purity. An analysis was made of the atmosphere of the tungsten furnace when it was operating at 2000°C. and a vacuum of 6 microns, as follows: H_2 , 86.5 per cent; N_2 , 8 per cent; CO, 3.5 per cent; CO_2 , 2 per cent.

Degassing in Arsem Vacuum Furnace.—Samples of molybdenum, 73 mils thick, caustic-dipped, were first degassed in an Arsem furnace, taken out, using care in handling, and degassed again in the quartz apparatus. The results are given in Table 7.

Tungsten Vacuum Furnace.—In order to obtain better vacuum than is possible in an Arsem furnace, an iron-jacketed vacuum furnace with a tungsten heater was set up. The heating unit consisted of a wire cage, of about 75 pieces of 80-mil tungsten wire, on supports of copper brazed in iron. The supports were water-cooled. The best vacuum obtained in this furnace was 5 microns measured on a Hale-Pirani gauge while the furnace was at 1950°C. and 2 microns at 1800°C. (Table 8.)

Hydrogen Firing.—It was found that samples fired in a tube hydrogen furnace at atmospheric pressure and 2000°C. gave off less gas on subsequent degassing than was present in unfired samples. The degassing time was not very different. (Table 9.)

It is noteworthy that hydrogen was not found in the gas from these hydrogen-fired samples. The explanation is to be found in the ease with which hydrogen comes off, so that undoubtedly it was given off during the 800° bake-out of the quartz and sample.

Experiments were then performed with purified hydrogen. The line hydrogen was passed through a liquid-air trap over heated platinized asbestos and through a second liquid-air trap. It was then led into the bottom of the quartz container and past the sample, at atmospheric pressure and a rate of about 4 c.c. per minute. The sample was kept heated by high frequency during this time. The quartz lead in tube was then sealed off, system evacuated and regular bake-out and degassing in vacuo followed.

TABLE 9.—*Gas from Hydrogen-fired Samples*
Hydrogen Fired in Tube Furnace at 2000°C.,
 $\frac{1}{2}$ hr. to 1 hr. Degassed at 1760°C.

Experiment No.	Degassing Time, Min.	Gas Composition, Per Cent			Amount of Gas, Cu. Mm. (NTP) per Gram Sample
		N_2	CO	CO_2	
304	16				0.86
305	25	91	9		0.97
306	25	70	30		1.00
300	20	81	16	3	1.07
301	25				1.20
288	25				1.20
302	20	59	36	5	1.20
284	45	63	29	8	1.50
292	20	95		5	1.70
Average....	25				1.15

In experiment 153 a sample was fired at 1600°C. for 1 hr. in purified line hydrogen at atmospheric pressure. On degassing it gave off 0.47 cu. mm. of gas per gram sample in 25 min., the gas being 89 per cent N_2 and 11 per cent CO. In experiment 156, another sample was fired in the same way at 1740°C. It evolved 0.39 cu. mm. of gas per gram sample, 16 per cent N_2 , 69 per cent CO and 15 per cent CO_2 .

Attempts were then made to obtain still purer hydrogen. A small, thin-walled

palladium tube was attached to the bottom of the quartz container by a graded seal. Surrounding this was a quartz tube, which had no connection to the quartz sample

Summary of Five Methods.—The five methods just discussed are summarized in Table 11. The "percentage of total gas removed," was calculated, taking 4.5

TABLE 10.—*Heating in Hydrogen Diffused through Palladium*

Heating in H ₂				Degassing Sample in Quartz				
Experiment No.	Pressure, Cm.	Temperature, Deg. C.	Time, Hr.	Temperature, Deg. C.	Gas Composition, Per Cent			Amount of Gas, Cu. Mm. per Gram Sample
					N ₂	CO	CO ₂	
138	50	1600	1	1070 1760	75	25		0.06 0.19
140	50	1740	1	1180 1760	61 60	39 36	4	Total 0.25 0.13 0.09
149	50	1740	1	1760	73	27		Total 0.22 0.07

container, but served to conduct hydrogen past the palladium tube. A small tube furnace surrounded it and was kept at 1100°C. At this temperature, hydrogen was able to diffuse through and past the molybdenum sample, which was heated by high fre-

quency. The pressure inside the system was kept at two-thirds of an atmosphere, to obtain a faster stream of hydrogen. In the best experiment, No. 149, the gas evolved is of the order of a monomolecular layer.

TABLE 11.—*Effect of Treatment of Molybdenum on Gas Content*

Method	Gas Left in Molybdenum, Cu. Mm. (NTP) per Gram Sample		Average Percentage, Total of Gas Removed
	Average	Lowest Value	
1. Hydrogen firing, tube furnace, 1 atm.....	1.15	0.86	72.7
2. Arsem vacuum furnace.....	0.95	0.58	78.1
3. Tungsten vacuum furnace.....	0.82	0.44	81.3
4. Purified line hydrogen, 1 atm.....	0.47	0.39	91.2
5. Line hydrogen diffused through heated palladium, at $\frac{3}{8}$ atm.....	0.16	0.07	95.8

quency. The pressure inside the system was kept at two-thirds of an atmosphere, to obtain a faster stream of hydrogen. In the best experiment, No. 149, the gas evolved is of the order of a monomolecular layer.

DEGREE OF VOLUME DEGASSING

The preceding experiments have suggested that the gas comes from the interior of the sample. This idea is supported when the time required for complete degassing is compared with the thickness of the sample (Fig. 7). The data in Fig. 7 are all for the standard sized ring, degassed at 1760°C. The fact that a volume and not a surface relationship is involved is also indicated by the relative change in thickness, surface area and degassing time in going from a 25-mil to a 250-mil sample.

These considerations led to a series of experiments in which a set of samples was made from 250-mil stock, cut down on a lathe to various thicknesses, taking equal cuts from each side. The samples were then degassed by standard procedure. Another set of samples of molybdenum was first degassed, the surface cut down to various depths, and the samples degassed

again. All were subjected to identical conditions as far as possible. All were from one stock piece of molybdenum. None was caustic-dipped to avoid heating, but

To degas tungsten at a rate comparable to that obtained with molybdenum at 1800°C . it is necessary to heat to 2300°C . It is interesting to note in experiment 172

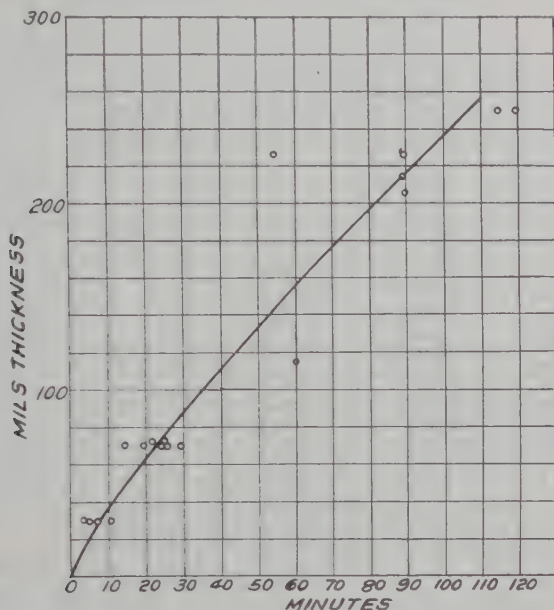


FIG. 7.—TIME OF COMPLETE DEGASSING FOR SAMPLES OF VARIOUS THICKNESSES. Molybdenum ring $\frac{7}{16}$ -in. inside diameter, $\frac{7}{8}$ -in. outside diameter, 1760° true temperature.

the scale on the original 250-mil piece was cut off on the lathe, bringing it to 227 mils. The samples were washed after cutting, in benzol then in alcohol and dried without touching.

The results are given in Fig. 8. These indicate that the degassing has reached about 90 mils = 0.090 in. into the sample, for at that point the amount of gas given off was the same whether or not the sample had a preliminary degassing.

The amount of gas present in the undegassed samples is proportional to the thickness of the sample, which is positive proof that we are dealing with gas inside the metal.

DEGASSING OF TUNGSTEN

Several tungsten rings were degassed in a high vacuum at temperatures ranging from 1400° to 2600°C . (Table 12.)

that further heating at 2610°C . produced no further gas evolution after degassing had been completed at 2430°C . The amount of gas obtained from a sample of tungsten ranges from 15 to 25 per cent of that obtained from a similar sample of molybdenum.

DEGASSING OF NICKEL

At 1030°C ., nickel has the same vapor pressure as molybdenum at 1760°C . (approx. 0.003 microns) and this is the highest temperature at which nickel can be maintained for a long period in a high vacuum without noticeable evaporation.

The first sample examined was taken from a nickel ingot which had been made from electrolytic nickel by vacuum-melting in an alumina crucible. The ring had an internal diameter of $\frac{7}{16}$ in. and an external

diameter of $\frac{7}{8}$ in. and was 250 mils thick. In 5 min. at 950°C . 1.76 cu. mm. gas per gram sample were evolved and in a subse-

quent 45 min., 1.02 cu. mm. The next sample was made from electrolytic nickel and was 71 mils thick. (Table 13.) The

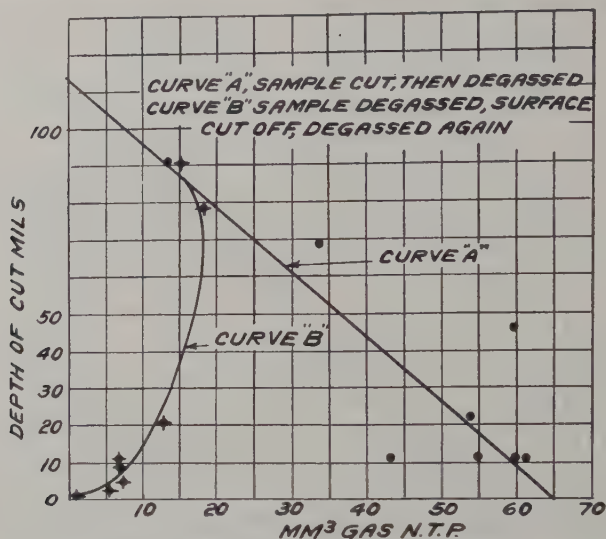


FIG. 8.—GAS EVOLVED AT VARIOUS DEPTHS.

Molybdenum ring $\frac{7}{16}$ -in. inside diameter, $\frac{7}{8}$ -in. outside diameter. Original 227 mils thick. 1760°C . true temperature.

TABLE 12.—*Degassing of Tungsten*

Total Gas Evolved, Cu. Mm. (NTP)	Percentage of Gas by Weight	Thickness, Mils.	Gas Cu. Mm. (NTP) per Gram Sample
5.94	0.000051	83	0.41
3.33	0.000029	83	0.23

sample in the last experiment evaporated more rapidly on one side than the other and finally melted at this spot and open circuited the ring.

For a further discussion of gas in radio metals, see E. M. Wise's paper on Nickel in the Radio Industry.⁸

AMOUNTS OF GAS EVOLVED FROM 14.5-GRAM TUNGSTEN SAMPLE

Experiment No.	Temperature, Deg. C.	Time of Heating, Min.	Composition of Gas, %				Total Gas, Cu. Mm. (NTP) per Gram Sample
			H ₂	CO	CO ₂	N ₂	
169	1410	15	7	35	5	53	0.07
	1740	50		22	13	65	0.19
	2140	35		57	2	41	0.11
	2490	25		100			0.04
Total.. 172	1440	20	1	41	7	51	0.41
	1740	50	9	44		47	0.07
	2130	25		9		91	0.10
	2430	20		40		60	0.05
	2610	15		100			0.01
Total..			3	30		67	0.23

GASES IN IRON

These were investigated by the previously described technique. After the rings were washed in alcohol and benzol to remove surface contamination, they were sealed in the apparatus. When a good vacuum had been attained, the whole was given a bake-out of 400° to 450°C . The metal sample was then degassed at temperatures from 850° to 1400°C ., and the gases given off in vacuum at different temperature levels were collected and analyzed. No oxygen was evolved as such in any experiment. At the higher tempera-

tures iron evaporation became troublesome. The types of iron used were:

1. Ordinary low-carbon stamping steel.

0.24 per cent; silicon, 0.34; sulphur, 0.010; phosphorus, 0.017; manganese, 1.29; molybdenum, 0.49.

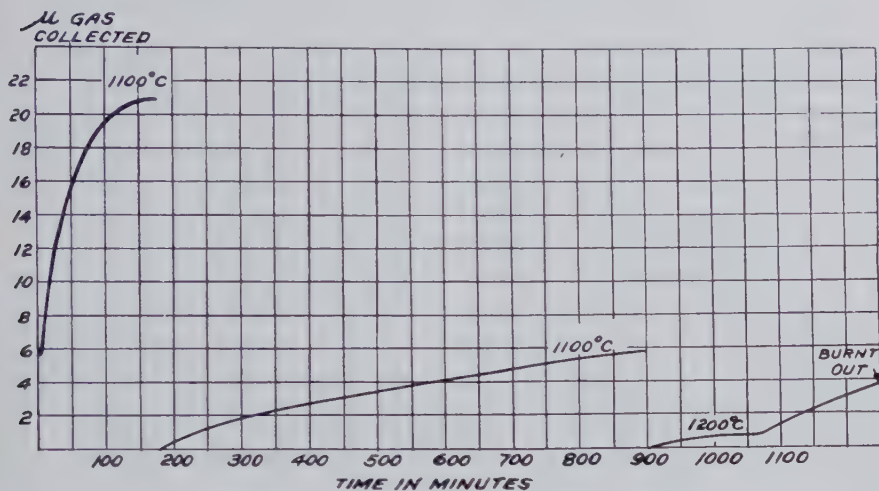


FIG. 9.—DEGASSING OF ELECTROLYTIC NICKEL.
 $I\mu = 2.8$ cu. mm. Sample weight, 4.5 grams.

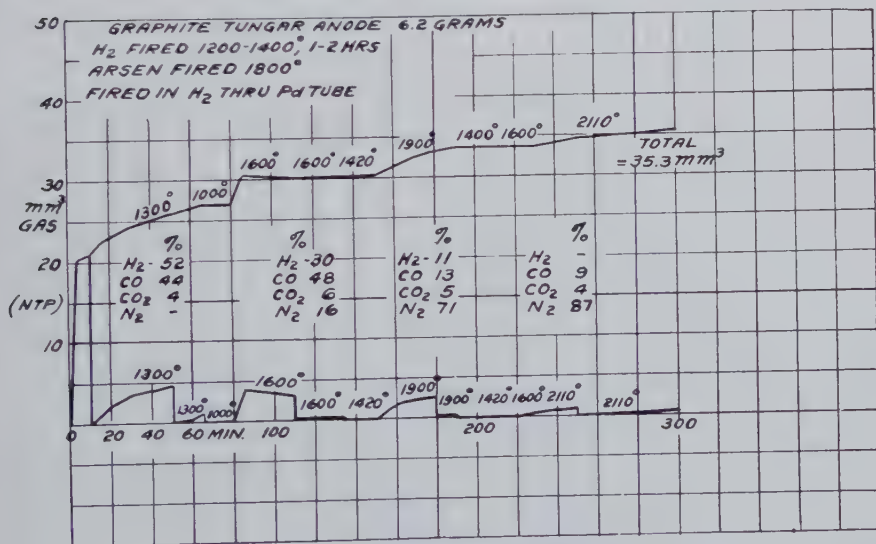


FIG. 10.—DEGASSING OF GRAPHITE.

2. Svea iron. This is described⁹ as "a special type of exceptionally pure Swedish iron made by a secret process to approach a chemically pure iron."

3. Cast steel. A manganese molybdenum steel with the following analysis: carbon,

0.17 per cent; silicon, 0.37; sulphur, 0.010; phosphorus, 0.019; manganese, 0.47; chromium, 1.74; molybdenum, 0.69.

5. "New iron" made by the General Reduction Corporation, Detroit. This

apparently was made by direct reduction of iron ore by gases, with subsequent pressing and sintering of the reduced iron. It shows many pores before and after

1800°C. Some of the samples were again fired in hydrogen in the degassing apparatus before degassing in an attempt to remove absorbed oxygen.

TABLE 13.—*Degassing of Nickel*

Temperature, Deg. C.	Time, Min.	Gas Composition, Per Cent				Amount of Gas, Cu. Mm. per Gram Sample
		H ₂	CO	CO ₂	N ₂	
RING 250 MILS THICK (16 GRAMS) Vacuum-melted Nickel						
950	5	13	65	15	7	1.76
	45	40	60			0.11
1050	35					0.18 no visible distillation
1170	20					0.14 distilla- tion of Ni
1090	400		90		10	0.59
Total.						2.78
RING 71 MILS THICK (4.5 GRAMS) Electro Nickel						
1100	177	2	77	10	11	13.1
	730		87	7	6	3.6
1200	240	14	75	4	7	2.6
Total.						19.3

degassing. This porosity and the probability of hydrogen pretreatment may have caused much of the dissolved gas to come out in our 450°C. vacuum prebake. By our regular procedure it gave the lowest gas content of the various iron samples. The composition of this "new iron" was: carbon, 0.05 per cent; silicon, 0.008; sulphur, 0.006; phosphorus, 0.008; manganese, 0.18.

The results on gases in these iron samples are summarized in Table 14.

DEGASSING OF CARBON

These experiments deal with the degassing of tungar anodes, which are made from Acheson graphite and are $2\frac{3}{32}$ -in. dia. and $\frac{1}{4}$ in. thick. The samples were all given a preliminary firing in a hydrogen furnace at 1500°C. and subsequently heated in an Arsem vacuum furnace at

TABLE 14.—*Gases in Iron*

Material	Temperature, Deg. C.	Gas, Cu. Mm. (NTP) per Gram Sample	Gases from Iron Analyses Per Cent			
			N ₂	CO	CO ₂	H ₂
1. Stamping steel, 5 mil, Expt. 229.	1060 1100 1200	520 110 70	0 9 20	100 78 58	0 4 14	0 9 8
Total.....		700				
2. Svea iron, 5 mil, Expt. 221	880 1030 1210	230 21 37	0 39 35	100 50 37	0 4 7	0 8 21
Total.....		288				
2. Svea iron, 62 mil, Expt. 166	980 1080 1200 1300 1380	13 40 159 12 6	0 35 51	95 61 41	5 4 8	0 0 0 0
Total.....		230				
3. Cast steel, 62 mil, Expt. 152	950 1000 1200	70 38 66	0 55 54	84 23 43	16 22 3	0 0 0
Total.....		174				
4. Bain steel, Expt. 155.	1115 1175 1220 1320 1430 1380	106 18 22 41 9	63 82 41 30 11	33 6 42 50 85	4 6 10 10 4	0 6 11 10 0
Total.....		155				
5. "New" iron, Expt. 160.	900 1078 1100 1347 1320 1316 1220 1300 1260 1255 1350	35 5 7 16 6 2 5 2 1 1 2	9 28 66	91 64 0	0 4 17	0 4 17
Total.....		82				
5. "New" iron, HF melted, Expt. 1.63.	950 980 1015 1110 1195 1240 1270 1280 1365 1370	2 5 2 3 14 5 7 18 9 5	46 32 85	32 22 0	0 10 5	0
Total.....		70				

At 2150°C. it is possible to degas graphite so that subsequent heating at a higher temperature gives no further gas. It is very interesting to observe that the gas

evolved in the range 1700° to 2200°C. is predominantly nitrogen. A piece of graphite which has been degassed completely on subsequent exposure to air absorbs oxygen and some of this is so firmly bound that it is only desorbed as carbon monoxide on subsequent heating to 2150°C. The results on graphite are given in Table 15.

ABSORPTION OF NITROGEN AND CARBON MONOXIDE BY MOLYBDENUM AND TUNGSTEN

A degassed sample of molybdenum was heated in the air by means of atomic hydrogen flame, which melted the edge of a sample entirely around the circumference, but left it still in the form of a ring. This

TABLE 15.—*Degassing of Graphite*

Experiment No.	Apparatus Firing					Degassing and Analysis					
	Impure H ₂	Pure H ₂	Pressure	Temperature, Deg. C.	Time, Hr.	Temperature, Deg. C.	Gas Analysis, Per Cent				Gas, Cu. Mm. (NTP) per Gram Sample
							H ₂	CO	CO ₂	N ₂	
206	*					1680 2090	40	51 23	3	9 74	1.3 0.5 Total 1.8
203	*					1640 2100	61	33 35	3	3 65	3.0 0.6 Total 3.6
273	*	*	50μ	1000	I	1330 1640 1950 2175	52 30 13	44 49 13 6	4 5 3 6	16 71 88	4.2 0.6 0.5 0.3 Total 5.6
256	*	*	40μ	1000	I	1020 1230 1330 1470 1640 1950 2160	74 64 56 43 53 17	15 24 26 17 6 13	4 I	7 12 17 40 41 70	1.8 3.3 2.2 0.4 0.5 0.3 0.3 Total 8.8
266	*	*	3 mm	1000	I	1020 1330 1640 1950 2140	64 69 84 2	10 28 4 9	12 3	14 12 86 91	5.4 4.0 2.3 0.3 0.3 Total 12.3
197	Previously degassed and exposed to air before degassing a second time.					980 1710 2130	73 31 49	65 4 32	4 4 4	23 15	0.2 0.3 1.0 Total 1.5

* Denotes treatment in column heading.

Very large amounts of gas were obtained from graphite that had not had the preliminary vacuum-furnace firing at 1800°C. One sample of graphite with pitch binder gave off 10,000 cu. mm. gas per gram sample. An unprocessed Acheson graphite yielded 270 cu. mm. gas per gram.

was then caustic-dipped and the regular degassing procedure applied. The sample then evolved 108.8 cu. mm. of gas at 1760°C. This gas was 96 per cent N₂ and 4 per cent CO₂. In the first 5 min. of heating in vacuo, 92 cu. mm. came off, and an hour longer was required for complete degassing.

In order to study more closely the taking up of gases by molybdenum and tungsten at high temperatures, a new series of experiments was performed. Degassed samples, 70 mils thick, were heated in the quartz chamber by high frequency in dry nitrogen and carbon monoxide, varying temperature, time of heating and pressure of the gas. The system was then pumped out, baked out if necessary, and the sample heated again in a very good vacuum, collecting and measuring the gas evolved from it.

For nitrogen it was found that no glow discharge appeared below 15 microns pressure or above 1 cm. pressure. All of these absorption experiments were performed in regions where no glow discharge appeared.

A detailed description of these experiments will be published elsewhere but a brief summary of the results may be of interest here. It has been found that the solubility of nitrogen in both tungsten and molybdenum is proportional to the square root of the nitrogen pressure. The variation of the solubility with temperature is represented by the equation

$$\frac{d \log (C^2/p)}{d(1/T)} = -\frac{\Delta H}{4.58}$$

where C is the solubility and p the nitrogen pressure. ΔH is the heat absorbed from the surroundings when 1 gram-mol of nitrogen is dissolved.

For tungsten $\Delta H = 74,700$

molybdenum $\Delta H = 38,500$

The solubility increases rapidly with increasing temperature.

The desorption of nitrogen from tungsten and molybdenum is a diffusion process and hence must obey Fick's law of diffusion

$$\frac{1}{K} \frac{dc}{dt} = \frac{d^2c}{dx^2}$$

This equation on integration shows that

$$\log \frac{a-x}{a} \propto Kt$$

and also that

$$\log \frac{dy}{dt} \propto Kt$$

If the logarithm of the rate of gas evolution at any fixed temperature is plotted as a function of time a straight line is obtained. The variation of the slope of this line as a function of temperature is determined by the variation of the diffusion constant with temperature.

$$\log K = \frac{A}{4.58T} + B.$$

For tungsten $A = -50,500$ cal.

molybdenum $A = -26,600$ cal.

At 1760°C. it was possible to saturate a 75-mil sample of molybdenum with nitrogen at 1 atm. pressure in 30 min. The time necessary for saturation with carbon monoxide appeared to be very much longer. For a 4-hr. heating period the amount of carbon monoxide absorbed was a linear function of time with no sign of saturation. At 1760°C. molybdenum absorbed in 30 min. eight times as much nitrogen as carbon monoxide and the nitrogen was desorbed in one-half the time taken by the carbon monoxide.

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DISCUSSION

L. L. WYMAN,* Schenectady, N. Y.—On page 359 there is a statement with reference to degassing, from which the impression might be gained that the table itself (Table 2) gives the impression that the gas is the same in each of the samples. Rather, it is a deductive affair; that is, when the difference in the cleaning operations and their effectiveness in taking off the gas are considered, it is evident that the basic amount of gas is about the same in all the samples.

* Research Laboratory, General Electric Company.

Diffusion in Relation to Changes in Microstructure

BY MARIE L. V. GAYLER*

(Chicago Meeting, October 1943)

WITHOUT diffusion taking place in liquid metals and alloys, no castings could be made; it is therefore the most important factor affecting the structure of metals. Diffusion involves the interchange of atoms, a process which takes place during the life history of an ingot. In the liquid, atoms are in a state of high thermal agitation, but this thermal vibration is reduced in amplitude with falling temperature. When solidification sets in, the atoms arrange themselves on an ordered space lattice and the changes in structure which take place in the solid are due to the interchange of atoms on this space lattice. The rate of atomic interchange—e.g., of diffusion—is most rapid at temperatures close to the melting point and decelerates as the temperature is lowered. At room temperature, the rate of diffusion is practically negligible in most alloys, and any change in structure can only be brought about by using methods which will accelerate the rate of diffusion.

The rate of diffusion depends on three factors (1) temperature; (2) concentration gradient and (3) activation energy. The growth of grains and particles in the solid alloy also depend on these factors and are therefore intimately associated with diffusion. The rate of homogenization in a cast alloy depends on several factors, such as: (1) rate of solidification, which involves

grain and particle size which, in their turn, depend on diffusion: (2) the nature of the constituents; (3) the temperature interval between the melting point of the metal or alloy and the temperature at which it is being heat-treated.

It is well known that coarse, cast structures are extremely difficult—if possible—to homogenize, and the finer the grain size and particle size, the more readily solid solution will take place. The rate of diffusion depends, also, largely on the nature of the constituents; for instance, copper and magnesium form solid solutions with aluminum quite readily but nickel and iron do not; neither do certain intermetallic compounds, such as α FeSi and β FeSi. Furthermore, the actual formation of intermetallic compounds may be a very slow process, particularly when they are formed in the solid state as equilibrium products. For example, β FeSi is formed in the solid as the result of the reaction $\alpha\text{FeSi} + \text{Al} \rightarrow \beta\text{FeSi}$. The particles of α FeSi become surrounded with a reaction ring of β FeSi. This layer is formed as the result of diffusion of atoms taking place between the aluminum matrix and α FeSi. As the amount of β FeSi surrounding the core of α FeSi increases the concentration gradient becomes low and so the rate of diffusion of atoms also decreases until it practically ceases. This occurs after a comparatively thin layer of β FeSi has been formed. It follows that when intermetallic compounds of this type are formed in the solid, as the result of diffusion, it is generally impossible ever to attain equilibrium, since the forma-

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*National Physical Laboratory, Teddington, England.

tion of the new phase inhibits further diffusion. This fact is particularly marked when large particles take part in the reaction; if the particle size is fine, however, it may be possible after prolonged annealing to cause the reaction to proceed to its limit. One means by which the reduction of particle size may be brought about is by working the material.

The interval between the temperature of melting of the alloy and that of heat-treatment has a definite effect on the rate of diffusion. The further the temperature of annealing is removed from that of melting, the less the rate of diffusion. In other words, diffusion in metals and alloys with high-temperature melting points generally takes place very slowly, if at all, at low temperatures—viz., room temperature—while those with low melting points diffuse with comparative ease. For example, the diffusion of nickel in iron at, say, $300^{\circ}\text{C}.$, is practically nil, while zinc diffuses readily in aluminum at the same temperature. Bound up with this ability to diffuse at room temperature is the atomic size of the atom, relative to that of the solute and, also, the vapor pressure of the element or compound. Metals with high vapor pressures, such as zinc and cadmium, diffuse readily.

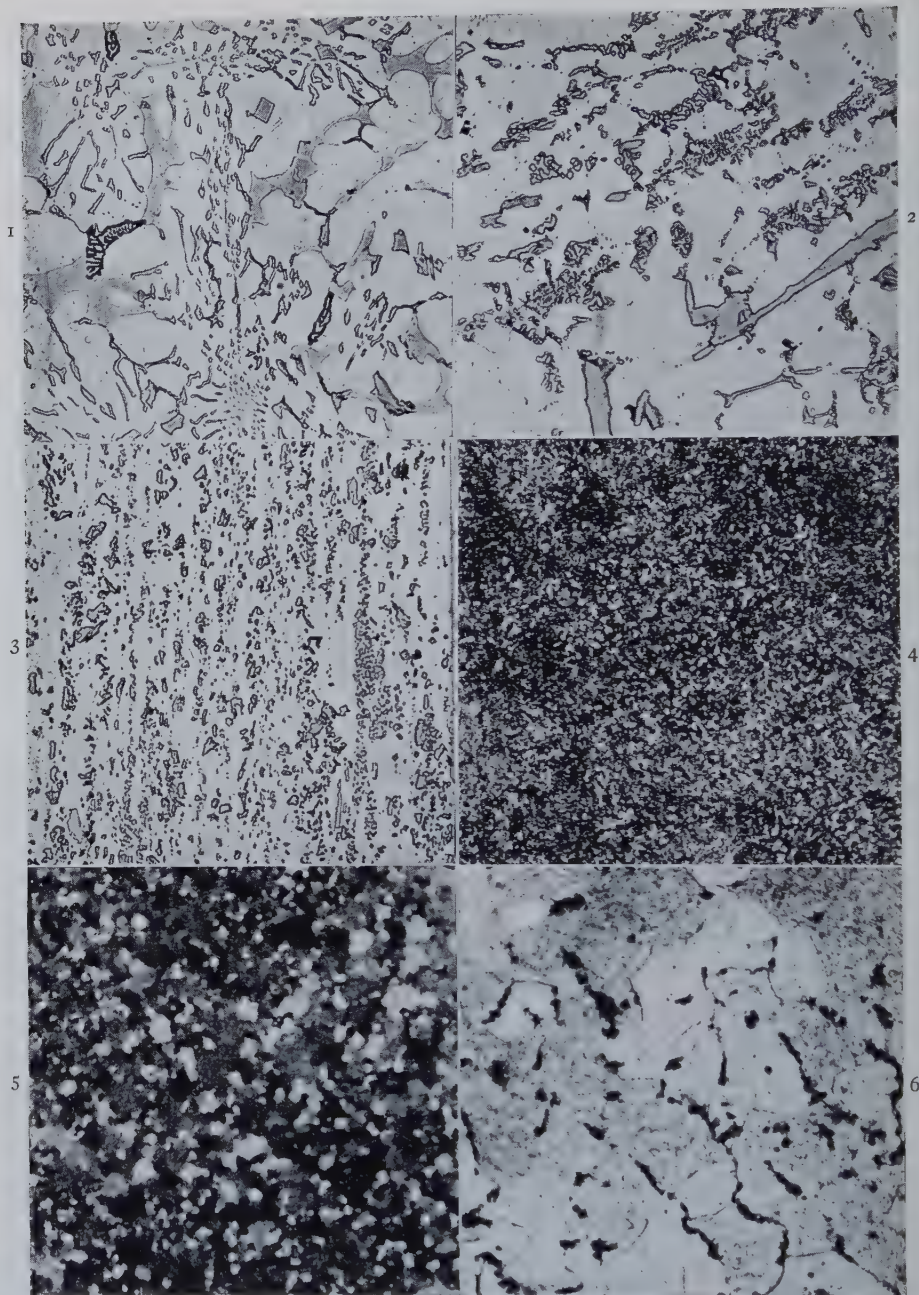
These few facts serve to show the importance of diffusion on cast structures; it is therefore of practical importance to consider ways by which the rate of diffusion can be accelerated if required. Rapid diffusion can be brought about by the following general methods; (1) suitable annealing; (2) hot-working; (3) cold-working followed by heat-treatment. It is proposed to discuss these three methods now very briefly.

ANNEALING OF CAST METAL

It is well known that annealing a cast alloy for a definite length of time at a specific temperature removes coring and causes partial absorption into solid solu-

tion of certain constituents present. In other words, the condition of the alloy is made to approach more nearly that of the equilibrium structure. The practical application of this phenomenon is of fundamental importance to the working of metals, since by its means apparently useless material can be made useful. For example, in certain alloys, eutectics exist which have low melting points; these prevent the casting being worked hot or cold. If the casting be annealed at a temperature close to that of the eutectic temperature, then, by the process of diffusion, the constituents of the eutectic can sometimes be made to be taken entirely into solid solution, or else the particle form is changed to a shape which is less harmful and which allows the alloy to be worked. For example, a 3-in. diameter billet of aluminum alloy containing 3 per cent Mg, 6 per cent Cu, 5 per cent Ni, cannot be hot-worked in the as-cast state satisfactorily. If the billet is annealed for one day at about $475^{\circ}\text{C}.$, the structure is changed and the billet becomes capable of being hot-pressed at that temperature down to a diameter of at least 1 in. Figs. 1 to 3 inclusive show the unetched structures, under a magnification of 150 diameters, of the cast, annealed and hot-pressed billet, respectively. The changes brought about in the casting, which have enabled it to be hot-pressed, have been due solely to diffusion in the casting.

Sometimes the presence of a small amount of liquid has no serious disadvantages. If residual, metastable eutectic is present in a cast alloy as a result of the rate of chilling, it is possible to cause rapid re-solution of the constituents of this eutectic by annealing at a temperature above that at which it melts. Diffusion then takes place very rapidly and the metastable eutectic disappears. The practical importance of this fact is that after such a short annealing the temperature

FIG. 1.—As cast. $\times 150$.FIG. 2.—Cast and annealed. $\times 150$.FIG. 3.—Cast, annealed and hot-pressed. $\times 150$.FIG. 4.—Copper-aluminum alloy containing iron. $\times 10$.FIG. 5.—Copper-aluminum alloy containing silicon. $\times 10$.FIG. 6.—Insoluble iron constituent in grain boundaries. $\times 250$.

can be quickly raised to any desired temperature for hot-working.

In the production of certain alloys by the powder metallurgy process, use is made of the fact that the rate of diffusion is accelerated by the presence of liquid, for the "binders" of various sintered products are formed by the melting of the constituent with the lowest melting point.

ANNEALING FOLLOWED BY HOT-WORKING

The mechanical properties of a chill-cast alloy can be considerably improved by hot-working following an annealing treatment. (The time and temperature of annealing depends entirely on the nature of the alloy in question.) The data of Table I illustrate this point. These results show

TABLE I.—*Annealing Followed by Hot-working*

	1-in. Diam- eter as Cast	1-in. Diam- eter as Cast, An- nealed 37 Hr. at 505°C.	3-in. Diam- eter Billet Annealed 37 Hr. at 505°C., then Hot- pressed at 500°C. Down to 1-in. Diameter
1 Per Cent Cu, 3 Per Cent Mg, Remainder Al			
Ultimate stress, tons per sq. in.	7	12	15
Elongation on 2 in., per cent...	4	7	24
1 Per Cent Cu, 3 Per Cent Mg, 5 Per Cent Ni, Remainder Al			
Ultimate stress, tons per sq. in.	7	9	17
Elongation on 2 in., per cent....	1	1	18
1 Per Cent Cu, 3 Per Cent Mg, 10 Per Cent Ni, Remainder, Al			
Ultimate stress, tons per sq. in.	9	10	16
Elongation on 2 in., per cent...	0.5-1	0	9

that by annealing—i.e., by the acceleration of the rate of diffusion—it has been possible to hot-work the cast alloy and thus improve its mechanical properties considerably.

COLD-WORKING FOLLOWED BY HEAT-TREATMENT

An important method of aiding diffusion is that of cold-working followed by suitable heat-treatment.

Allotropic transformations in many metals may be suppressed or raised by the addition of another element. For instance, it is well known that in certain ferrous alloys the $\gamma\text{Fe} \rightarrow \alpha\text{Fe}$ transformation does not take place on cooling down to room temperature. Such an alloy is then in a metastable state and if the transformation proceeds only very slowly at room temperature, this may be disadvantageous practically. Suppressed transformations can generally be made to take place if the alloy be cold-worked but it is not always possible to cold-work completely such an alloy, since, owing to the increased hardening which occurs as soon as the transformation is started (as in certain ferrous alloys) further cold-working is prevented. If, however, cold-working is possible, a subsequent annealing will generally accelerate the rate of change of transformation.

Apart from accelerating allotropic transformations, cast alloys are very often homogenized by means of cold-working followed by annealing or by hot-working. In either case grain refinement occurs with marked improvement in mechanical properties. Such treatments allow diffusion to take place readily and the final structure approximates to that under equilibrium conditions and generally consists of a refined grain, the size of which depends on the temperature of heat-treatment.

Given the same heat-treatment, variation in the grain size of a worked alloy may be brought about by additions of certain elements which form insoluble constituents. The presence of these phases appears to act as a mechanical hindrance to grain growth and, in that sense, prevents diffusion taking place freely. For instance, the addition of 0.2 per cent iron to high-purity 4 per cent copper-aluminum alloy

has an entirely different effect from that caused by the addition of 0.2 per cent silicon. If these two alloys be cold-forged and annealed for 2 hr. at 500°C., the etched structures are obtained, as shown in Figs. 4 and 5, respectively, under a magnification of 10 diameters. In the former case the grain size is small, while that of the second is comparatively coarse. Under a higher magnification (Fig. 6), it is seen that the insoluble iron constituent lies more or less in the grain boundaries. In the alloy containing 0.2 per cent silicon, this element is capable of being held in solid solution in aluminum and any out of solution does not appear to affect the grain size.

SUMMARY

Diffusion in metals and alloys is a process without which little use could be made of much available material: the rate of

diffusion can be accelerated by various well-known methods.

DISCUSSION

E. A. ANDERSON,* Palmerton, Pa.—In regard to the mention of the ability to diffuse at room temperature (p. 373), I might say that aluminum diffuses very readily in zinc at room temperature. Preceding the words, "Cold-working followed by heat-treatment, an important method of aiding" (p. 375), I believe Dr. Gayler would wish to interpolate a comment on a possible misunderstanding of the meaning of the data in column 3. I do not believe she means to infer that the increased diffusion brought about is responsible solely for the higher values. I think she probably wishes to infer that the improvement due to changed grain size and recrystallization brought about by hot-working is made possible by having had the diffusion precede the hot-working.

* Research Division, The New Jersey Zinc Company.

Diffusion in Alclad 24S-T Sheet

By F. KELLER* AND R. H. BROWN,* MEMBER A.I.M.E.

(Chicago Meeting, October 1943)

BECAUSE of the extensive use of Alclad 24S alloy sheet in aircraft construction, there is much interest in the metallurgical changes caused by heat-treatment of this product.^{1,2} One of these changes is the result of the diffusion of soluble elements from the core into the coating during treatment. This paper deals with the thermal treatments that may influence diffusion and with the practical effects of diffusion on the serviceability of the product.

As is well known, Alclad 24S-T sheet has a core of high-strength alloy combined with surface layers of relatively pure aluminum. The microstructure of a cross section of this product is shown by Fig. 1. Not only does the relatively high-purity coating have a high resistance to corrosion, and hence serves as a mechanical barrier between the core metal and the corroding environment, but in addition this coating exerts electrochemical protection over areas where the core may be exposed, such as cut edges. In addition, the coating affords electrochemical protection to projecting heads of Al7S-T, 17S-T and 24S-T rivets, or attached members made from these alloys. Under some conditions of heat-treatment, however, diffusion of copper into the coating will alter the electrochemical relationship between the coating and the core to the extent that

only partial protection will be obtained under some corrosive conditions.

The reason for the electrochemical protection lies in the fact that the coating layers of pure aluminum are anodic to the alloy core. The addition of copper to aluminum produces alloys in which the potential is lower than that of the pure metal. Moreover, as the amount of copper in solid solution in 24S alloy is increased, the potential of the alloy becomes more cathodic. When heat-treated at 920°F. and quenched in cold water, 24S-T is about 0.16 volt cathodic to pure aluminum. However, copper will diffuse from the core into the coating, and if it reaches the surface the potential will be altered in a cathodic direction. Thus the potential difference between the core and coating may be less than 0.16 volt, depending upon the thickness of the coating, and the time and temperature of heat-treatment.

Of the methods available for determining the extent of diffusion of copper from the core into the coating of Alclad 24S-T, two are generally used; namely, the metallographic and the solution potential methods.³

METALLOGRAPHIC METHODS

Metallographic methods will reveal the progress of diffusion of copper into the coating. For instance, the diffusion zone in the coating intermediate between the coating surface and the core is shown in Fig. 1. This photomicrograph is of a polished and etched cross section of 0.040-in. Alclad 24S-T sheet. Diffusion proceeds into the coating more rapidly along the grain boundaries than through the body of the grains. Consequently, the diffusion zone is not of uniform width

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* Aluminum Research Laboratories, New Kensington, Pa.

¹ References are at the end of the paper.

but appears in a cross section as a series of peaks and valleys, as shown by the sketch in Fig. 2.

Examination of polished and etched cross sections of Alclad 24S-T sheet will show how far the diffusion has progressed



FIG. 1.—FULL CROSS SECTION OF SAMPLE OF ALCLAD 24S-T, 0.040 INCH THICK. $\times 100$. KELLER'S ETCH.⁴

The relatively pure aluminum coating, the diffusion zone, and the 24S-T core are evident.

into the coating, but it will not give much information about the actual amount of copper that has diffused into the coating or to the surface of the coating. However, an approximation of the copper content at the surface of the sheet can be obtained by examining surfaces prepared with carefully controlled etching methods.⁴ If no copper has reached the surface of the sheet as a result of diffusion, the microstructure of the coating will not be developed by these treatments. If, however,

diffusion has reached the surface at the grain boundaries but not within the grains, a cellular network similar to that shown in Fig. 3 will be revealed. When both peak and valley diffusion have reached the surface of the coating, the grain

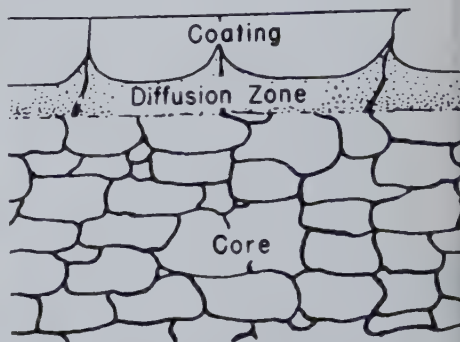


FIG. 2.—PEAK AND VALLEY NATURE OF DIFFUSION ZONE IN ALCLAD COATING.

boundaries will be thin and sharply defined and grain contrast will be evident. The changes in the microstructure of the surface of the alclad coating resulting from different amounts of diffusion are shown by Figs. 3 to 6 inclusive.

SOLUTION POTENTIAL METHOD

Solution potential measurements are employed to estimate quantitatively the amount of copper that diffuses to the surface of alclad coatings. In brief, the solution potential as used in this paper is the potential of a cell composed of the sample as one electrode, a 0.1 normal calomel electrode as the other electrode, and a solution containing 53 grams of sodium chloride and 3 grams of hydrogen peroxide per liter as measured on a null instrument such as a potentiometer. As mentioned⁵ previously, the potential of an aluminum-copper alloy is a function of the amount of copper in solid solution. The effect of copper in solid solution on the potential of an alloy base of the same composition as the coating on Alclad 24S-T is shown by curve *A* in Fig. 7. Curves *B* and *C*, one for 0.016 in. and the

other for 0.064-in. Alclad 24S-T sheet, show the effect of time of heat-treatment at 920°F. on the potential at the surface of the coatings on material quenched in

to the measured value of the potential of the alclad coating.

Fig. 8 shows the amount of copper diffused to the surface of alclad coatings

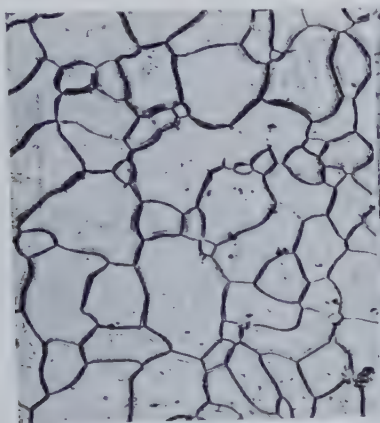


Fig. 3. Diffusion to surface of alclad coating along grain boundaries in a sample of 0.016-in. alclad 24S-T sheet which had been heat-treated for 5 min. at 920°F.

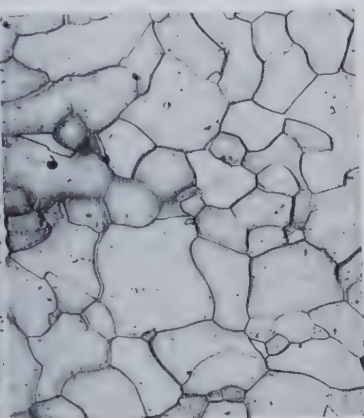


Fig. 4. Structure of surface of coating on same material with a 15-min. heat-treatment.

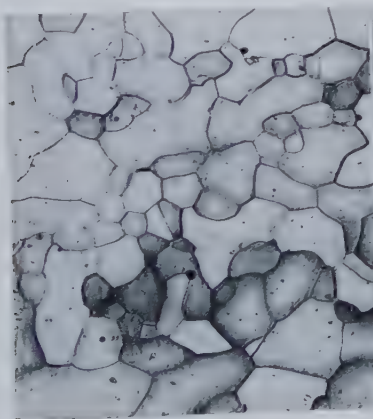


Fig. 5. Structure of surface of coating on same material with a 30-min. heat-treatment.

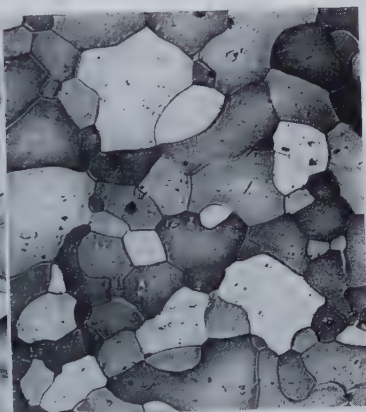


Fig. 6. Structure of surface of coating on same material with a 60-min. heat-treatment.

FIGS. 3-6.—MICROSTRUCTURE OF SURFACE OF COATING OF ALCLAD 24S-T SHEET. $\times 100$.

The surface sections were etched exactly 60 seconds in Keller's etch. The depth of color developed in the microstructure is an indication of the amount of copper that has diffused to the surface of the alclad coating.

cold water. The copper content at the surface of alclad coatings can be obtained by taking the values from the curve for the aluminum-copper alloys corresponding

as determined by the potential method. The variables are time and temperature of heat-treatment, and coating thickness. The coatings on all of the different thick-

nesses of sheets were 5.5 per cent of the total thickness on each surface. Fig. 9 shows the effect of sheet thickness on the concentration of copper at the coating

EFFECTS OF DIFFUSION ON THE CORROSION OF ALCLAD 24S-T

Diffusion proceeds faster at the grain boundaries than through the grains them-

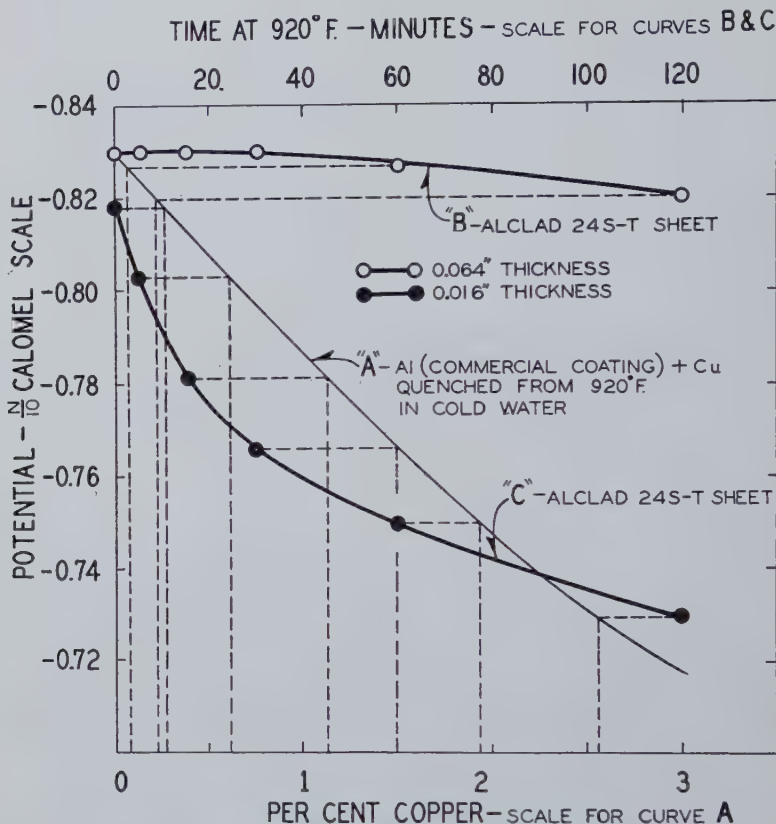


FIG. 7.—SHOWS METHOD OF DETERMINING AMOUNT OF COPPER AT SURFACE OF ALCLAD 24S-T SHEET BY MEANS OF POTENTIAL MEASUREMENTS.

The copper content at the surface of the alclad coating is obtained by projecting the measured potential of the coating as indicated by the dotted line until it intersects curve A and reading the corresponding copper content as indicated.

surface after three periods of heat-treatment. From these data it can be seen that below 650°F. diffusion is negligible even for the thinnest material. Even at the highest temperature (930°F.) the copper that reaches the surface of Alclad 24S-T sheet 0.032 in. or over in thickness will have no practical effect even though the material is heat-treated for periods appreciably longer than those recommended.

selfes; therefore, the copper content at the surface of the coating at the grain boundaries will be appreciable before any copper has reached the surface at the central surface areas of the grains. Solid solutions high in copper are cathodic to solid solutions lower in copper; consequently, the grain-boundary zones in a partly diffused alclad coating will be cathodic and the central surface areas will

be anodic. Upon exposure of an alclad specimen in the above condition to a corrosive environment, this distribution

micrograph in Fig. 11, on a specimen of Alclad 24S-T that was exposed in a corrosive environment. Note that the zones

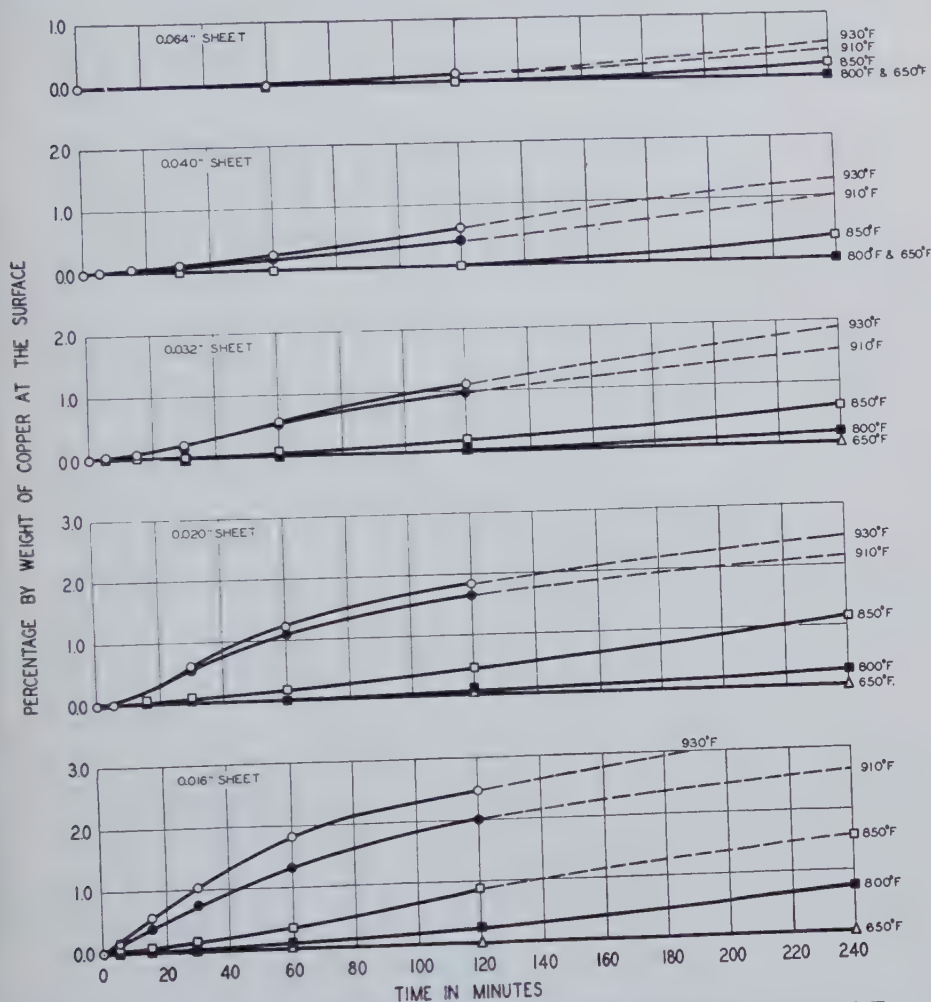


FIG. 8.—SHOWS AMOUNT OF COPPER DIFFUSED TO SURFACE OF COATING ON ALCLAD 24S-T SHEET AS DETERMINED BY THE POTENTIAL METHOD.

The periods and temperatures of heat-treatment and the thicknesses of the sheet are indicated on the chart. The coatings were 5.5 per cent of the total sheet thickness on each surface for all gauges.

of the anodic and cathodic areas would cause the central surface areas of the grains to corrode and electrochemically protect zones along grain boundaries. This distribution of corrosion is illustrated diagrammatically in Fig. 10 and in a photo-

along the grain boundaries are ridges and at the center of the grains are valleys.

Since the concentration of copper in a diffused alclad coating will progressively decrease from the interface to the surface, any corrosion of the coating will expose

metal that will be anodic to the remaining metal beneath it. Consequently, the metal at the surface electrochemically protects the metal in the diffusion zone and in

still longer exposure, the corrosion will progress to the core alloy and again spread out. In Alclad 24S-T sheet that has been rapidly quenched from the heat-treating

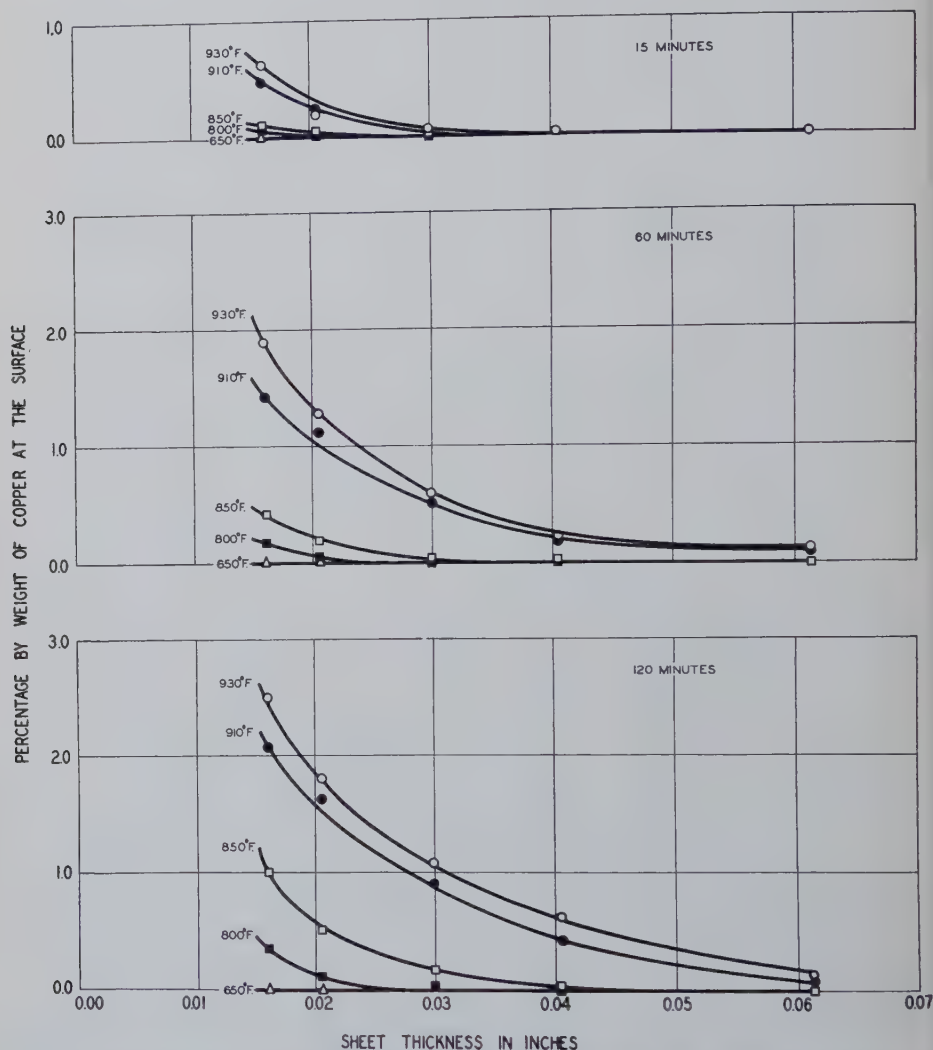


FIG. 9.—SHOWS EFFECT OF SHEET THICKNESS ON CONCENTRATION OF COPPER AT SURFACE OF ALCLAD 24S-T SHEET AFTER THREE DIFFERENT PERIODS OF HEAT-TREATMENT.

turn the diffusion zone electrochemically protects the core alloy. Hence, in Alclad 24S-T sheet in which diffusion has occurred, corrosion will progress, at first, to the diffusion zone and spread out rather than penetrate into the diffusion zone. Upon

temperature, corrosion will penetrate to the interface but not into the core because of the electrochemical protection afforded the core by various portions of the coating as long as part of the coating remains.

The greater the extent of diffusion, the more nearly the potential of the coating will approach that of the core. Moreover, since the amount of copper retained in

core and coatings of Alclad 24S-T sheet 0.016 in. thick, heat-treated for several periods of time and quenched at several different rates. In addition, one series of



FIG. 10.—APPEARANCE OF HILL AND VALLEY CORROSION ON SURFACE OF PARTIALLY DIFFUSED ALCLAD 24S-T SHEET.

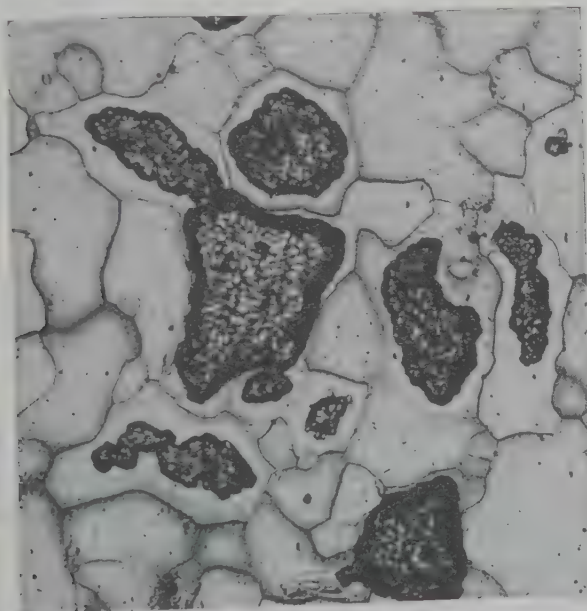


FIG. 11.—SURFACE OF PARTIALLY DIFFUSED ALCLAD 24S-T SHEET, 0.020 INCH THICK, AFTER EXPOSURE OF 72 HOURS IN STANDARD SODIUM CHLORIDE-HYDROGEN PEROXIDE TEST. KELLER'S ETCH. $\times 100$.

Note that attack has occurred at the center of the grains, as was shown diagrammatically in Fig. 10.

solid solution is affected by the rate of quench, it follows that the potential of the core also will be affected by the rate of quench. In addition, the type of attack to which the 24S-T core is susceptible is determined by the rate of quench. In Fig. 12 are shown the potentials of the

Alclad 24S-T sheet 0.020 in. thick was included for comparison. The slower the rate of quench, the greater is the tendency toward susceptibility to intergranular attack. The core of the sheet that was quenched in cold water was susceptible to pitting attack when the coating was

removed before testing, whereas the core of the material that was quenched in boiling water was susceptible to intergranular attack, and the latter was true also for still slower rates of quench.

In Fig. 13 the potential difference between coatings and core is plotted against the change in tensile strength caused by the exposure of 0.016-in. Alclad 24S-T sheet in the corrosion test. Although

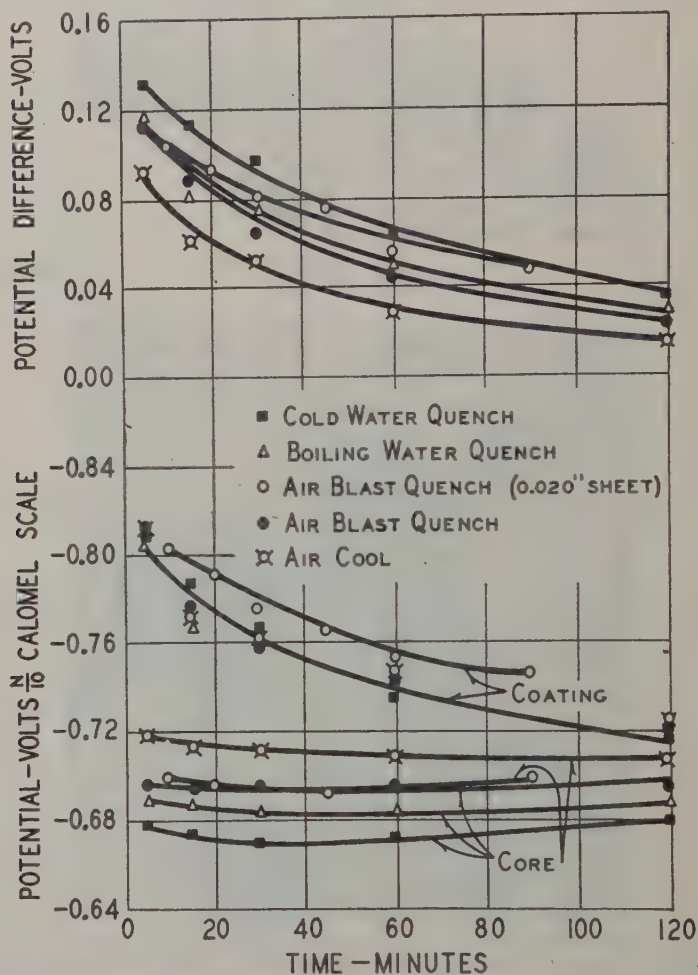


FIG. 12.—SHOWS EFFECT OF RATE OF QUENCH AND TIME OF HEAT-TREATMENT AT 920°F. ON POTENTIAL RELATIONSHIPS BETWEEN COATING AND THE CORE OF ALCLAD 24S-T.
 * All material was 0.016 in. thick, except as noted.

In order to evaluate the resistance to corrosion, the 0.020-in. thick Alclad 24S-T materials were exposed in the standard sodium chloride-hydrogen peroxide alternate immersion test. The results of these tests are summarized in Table 1.

the diffusion of copper into the coating reduced the potential difference between the coating and core, the diffusion has not caused an increase in corrosion losses, provided the material was quenched in cold water. However, with slower rates

of quench the increased diffusion causes avoided if 0.016-in. thick alclad sheet is an increase in the corrosion losses. For quenched in boiling water.

TABLE 1.—*Effect of Quenching Rate on the Resistance to Corrosion of Thin-Gauge (0.020-Inch) Alclad 24S-T Sheet*

Heat Treatment*		Mechanical Properties			Solution Potential		Potential Difference	Copper at Surface, Per Cent	Resistance to Corrosion ^b	
Time, Min.	Quench	Tensile Strength, Lb. per Sq. In.	Yield Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent	Of Coating	Of Core			Change in Properties, Per Cent	
									Tensile Strength	Elongation
12	Cold water	63,630	39,050	20.0	0.814	0.680	0.134	0.27	-5	-33
60	Cold water	64,810	40,050	20.5	0.782	0.677	0.105	0.85	-7	-18
12	Boiling water	63,950	39,450	20.3	0.800	0.687	0.113	0.52	-4	-26
60	Boiling water	64,010	40,000	20.8	0.775	0.686	0.089	1.00	-6	-21
12	Air blast	62,860	36,950	19.5	0.817	0.690	0.127	0.22	-2	-6
60	Air blast	64,660	40,350	20.5	0.784	0.695	0.089	0.80	-25	-77
12	Air cool	60,390	36,200	19.3	0.814	0.716	0.098	0.27	-30	-82
60	Air cool	61,390	36,850	19.5	0.783	0.712	0.071	0.82	-62	-90

* Samples heat-treated as 8 by 10-in. panels in Homo Furnace at 920°F. Air-blast velocity, 110 ft. per second.

^b 48-hour alternate immersion test using sodium chloride-hydrogen peroxide solution.

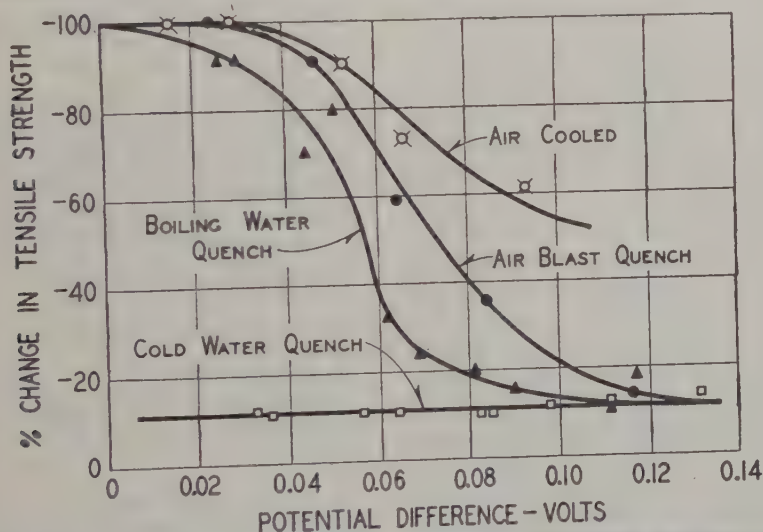


FIG. 13.—SHOWS CORRELATION OF CHANGES IN MECHANICAL PROPERTIES RESULTING FROM CORROSION WITH POTENTIAL DIFFERENCES BETWEEN CORE AND COATING.

Corrosion tests were made on 0.016-in. thick Alclad 24S-T sheet by exposure to standard sodium chloride-hydrogen peroxide alternate immersion test for 72 hours.

example, periods of heat-treatment of such duration that the diffusion reduced the potential difference between the coating and core to less than 0.08 volt should be

OTHER EFFECTS OF DIFFUSION

When appreciable amounts of copper diffuse to the surface of the coating of Alclad 24S-T sheet as a result of pro-

longed heat-treatment, the coating will tend to become darkened and discolored. This does not mean that the product will not be serviceable, unless the heat-treating practices have been such that the proper potential relations between the coating and the core are not maintained. From the appearance standpoint, however, stained and discolored sheet may not match adjacent material in structure.

Another instance where diffusion of copper to the surface of the coating may be of some significance is in connection with the spot welding of Alclad 24S-T sheet. One of the important factors in connection with spot welding is the cleaning of the sheet surface prior to welding. Material that has different amounts of copper diffused to the surface may not respond uniformly to some types of cleaning treatment.

SUMMARY

From the results that have been obtained by the metallographic and solution potential methods described in this paper, it is evident that very little copper will reach the surface of Alclad 24S sheet by diffusion when a temperature of 800°F. or lower is employed. Thus, any treatments used for annealing or aging will not cause a significant amount of diffusion. In Alclad 24S-T material heat-treated in the normal temperature range, 910° to 930°F., considerable copper will diffuse to the surface in an unduly long heat-treatment for any given thickness of material. Amounts of copper at the surface of the order of those shown will not affect the resistance to corrosion of the material if a sufficiently rapid rate of quenching is employed. When material is quenched under the less rapid conditions noted in this paper, the amount of diffusion

to the surface will be important if it changes the potentials to the point where adequate electrochemical protection is no longer obtained. It is assumed that when Alclad 24S-T is not quenched rapidly, the heat-treating conditions will be controlled to keep the amount of diffusion as low as possible and adequate protective measures will be taken against the possibility of corrosive action.

ACKNOWLEDGMENTS

The authors wish to acknowledge the many contributions made by various members of the Aluminum Research Laboratories, especially those by Messrs. J. A. Nock, Jr. and M. S. Hunter.

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DISCUSSION

H. R. KING,* Buffalo, N. Y.—What is considered a rapid time for quenching—in seconds? What would be considered an ideal time for quenching?

F. KELLER (author's reply).—In commercial heat-treatment, less than 15 sec. would be considered rapid.

* Metal and Alloy Specialties Co., Inc., Buffalo, N. Y.

Diffusion of Indium in Bearings

By A. A. SMITH, JR.,* MEMBER A.I.M.E.

(Chicago Meeting, October 1943)

THE application of indium to bearings was first advocated by C. F. Smart¹ in 1938, for the purpose of inhibiting corrosion of certain bearing alloys. He found that a thin layer of indium plated on the bearing surface and subsequently diffused at elevated temperatures markedly decreased the rate of corrosion in lubricating oils containing organic acids. Most of his work was done on cadmium-base alloys, although he showed that the treatment was also effective for copper-lead and other alloys. Since their introduction, indium-treated bearings have found considerable use, particularly in connection with airplane motors.²

Undoubtedly the effectiveness of the indium plate in resisting corrosion depends upon its relative concentration on the bearing surface after the diffusion treatment and after prolonged use at operating temperatures. Some diffusion experiments were made on a number of base metals that had been indium plated, to determine the depth of penetration after heating for reasonably long periods of time. As only the practical aspects were desired, no attempt was made to determine actual diffusion constants.

METHOD

Two different series of experiments were carried out to study the diffusion of indium

into several base metals. Cast cylinders about one-inch diameter were machined to 0.750-in. diameter, so as to remove all surface imperfections, and final finishing was done with 00 sandpaper. The original diameters were very carefully measured with micrometers and then a layer of indium was electrolytically deposited on the cylinders from a sulphate bath.³

In the first series of experiments, about 0.002 in. of indium was deposited and diffusion was carried out at 150°C. for a period of 500 hr. in a thermostatically controlled electric oven. After the diffusion period, successive layers were machined from the specimens and analyzed spectrographically and chemically—the spectrographic examination serving as a guide to determine which layers should be chemically analyzed.

Apparently there was some surface oxidation of the indium plate due to the long heat-treatment, which may have had some effect on the diffusion. Also, the cadmium alloy showed some incipient melting, which probably was caused by the formation of a low-melting eutectic. To eliminate these factors, another series of experiments was carried out by heating in an electrically heated, automatically controlled, oil bath at lower temperature. The preparation of the specimens was the same as before except that a layer of indium 0.0001 in. thick, an amount commonly used commercially on bearings, was deposited on each of the cylinders. Diffusion was carried out at 120°C. for a period of 200 hours.

Presented as part of the Symposium on Practical Aspects of Diffusion. Manuscript received at the office of the Institute July 22, 1943. Issued as T.P. 1640 in METALS TECHNOLOGY, December 1943.

* Central Research Laboratory, American Smelting and Refining Co., Barber, New Jersey.

¹ References are at the end of the paper.

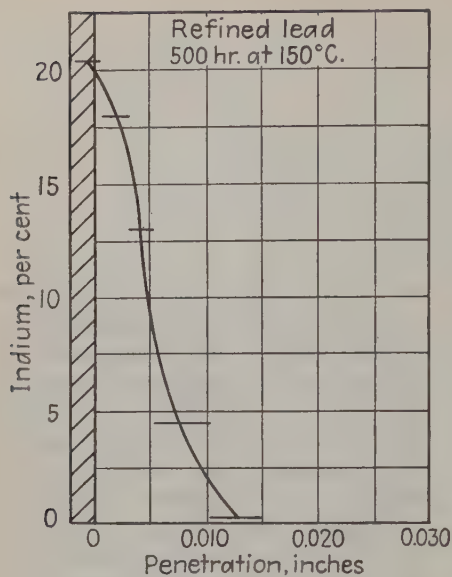


FIG. 1.

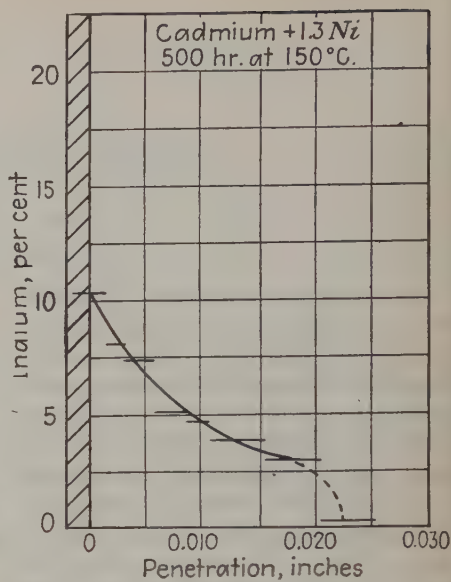


FIG. 2.

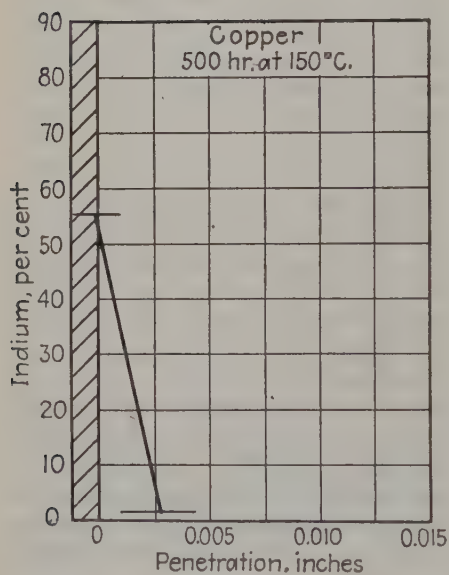


FIG. 3.

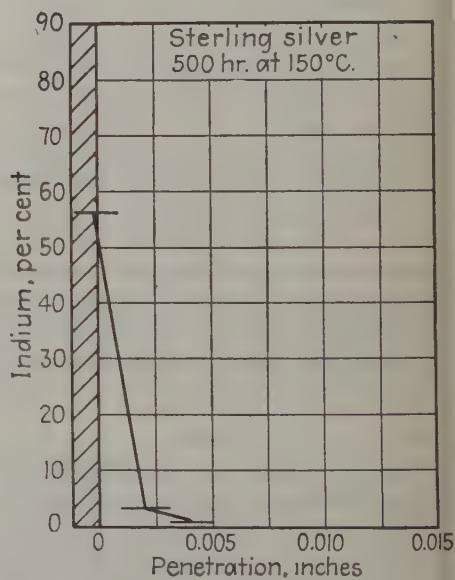


FIG. 4.

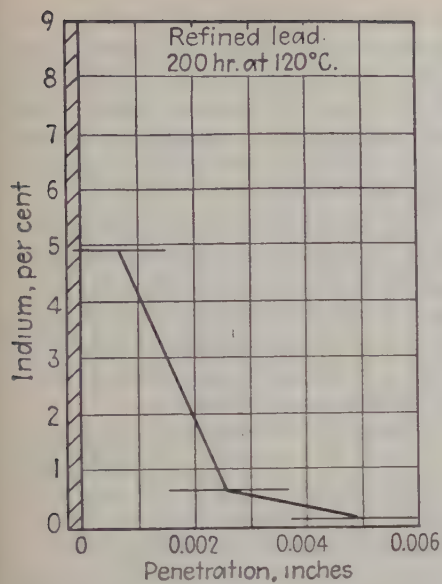


FIG. 5.

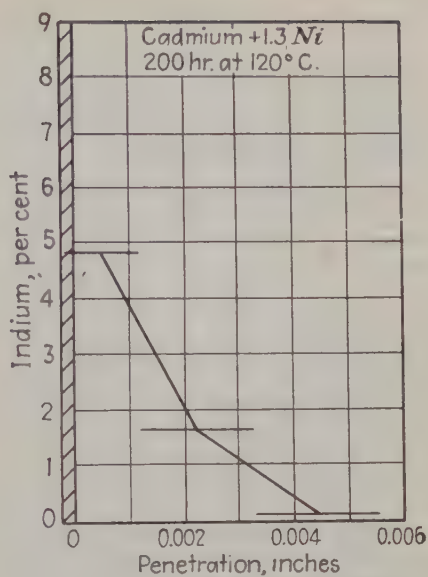


FIG. 6.

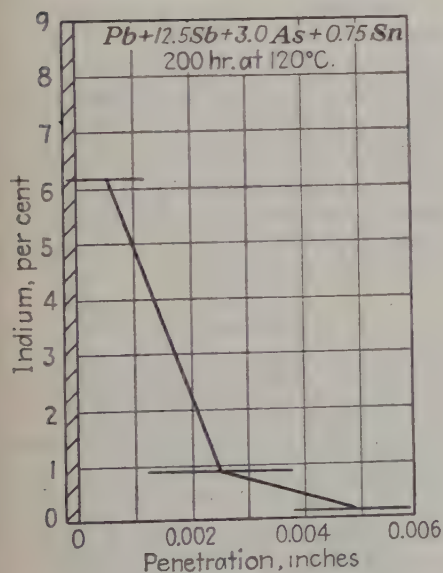


FIG. 7.

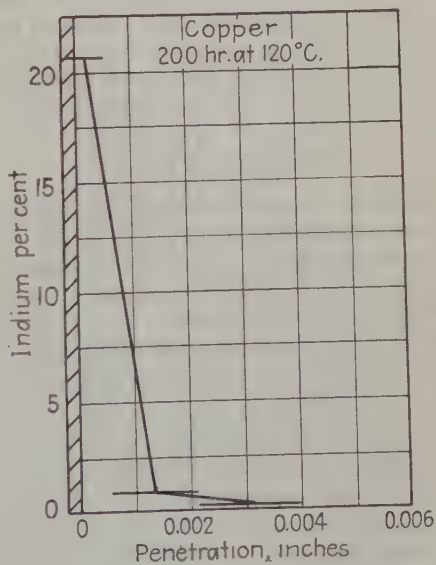


FIG. 8.

DATA

Table 1 lists the various alloys and the exact thickness of the indium plate, this thickness being the average computed from weight and area measurements.

TABLE 1.—*Thickness of Indium Plate*

No.	Alloy	Thick- ness of Plate, In.	Series No.
1	Refined lead (99.99)	0.00197	1
2	Cadmium + 1.3 Ni	0.00220	1
3	Oxygen-free copper	0.00242	1
4	Sterling silver	0.00212	1
5	Refined lead (99.99)	0.00011	2
6	Cadmium + 1.3 Ni	0.000097	2
7	12.5 Sb, 3.0 As, 0.75 Sn, bal. Pb	0.0001	2
8	Oxygen-free copper	0.00008	2

In Figs. 1 to 8 are plotted the percentage of indium versus the distance from the original surface of the sample; i.e., the interface between the indium and the base metal being the zero abscissa. The length of the horizontal line indicates the thickness of the analyzed layers. To the left of the interface, the shaded area represents the original indium plate. (In Figs. 5 to 8 the shaded areas are not to scale because of the extreme thinness of the indium plate.)

DISCUSSION OF RESULTS

The location of the original interface between the two metal layers is difficult to determine in diffusion experiments because of possible dimensional changes and errors in measurement. It is probable that such errors are found in the present work, although it is felt that they are not serious from the practical point of view.

In series 1, calculation of the amount of indium present after the diffusion treatment indicates that some indium was lost through oxidation, or, in the case of cadmium, run off by melting. This did not occur in series 2, as the indium can be accounted for within the accuracy of measurement and analysis.

In both series of experiments the depth

of diffusion of indium is greatest in the cadmium alloy, followed by the lead alloys. With copper and sterling silver the depth of penetration of indium was relatively slight, the concentration approaching zero at only a few thousandths of an inch from the interface.

The constitutional diagrams for copper-indium,⁴ silver-indium,⁵ and lead-indium^{6,7} indicate a large solid solubility of indium, the solid solubility of indium in cadmium has not been determined⁸ but undoubtedly there is an appreciable amount, as indicated by the diffusion experiments.

Because of the limited number of diffusion data and the lack of precise solid solubility limits in indium alloys, the calculation of diffusion constants appears questionable and of little value.

In all cases the concentration of indium at the surface remains relatively high even after the more drastic diffusion experiments. Smart¹ has indicated that even as low as 0.37 per cent indium alloyed with cadmium-bearing metals will markedly decrease the rate of corrosion in acidified lubricating oils. If that is true, these data indicate that extremely long times would be necessary before diffusion would progress to such an extent that the indium content at the surface would be below this amount, assuming that the weight of indium is less than 0.4 per cent of the weight of the base metal.

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DISCUSSION

C. F. SMART,* Pontiac, Mich.—It is very gratifying that the author's data on the diffusion of indium in cadmium alloy and in lead bear out the results of indium treatment of bearings containing these metals.

A word of caution, however, may be in order—experience has indicated that dependence for corrosion resistance should not be placed on relatively high indium concentration remaining in the surface layers. This is somewhat contrary to the author's conclusion as stated in the final paragraph of his paper. At first thought this may appear confusing, but examination of the differences between bearing practice and the author's work offers an explanation.

Our investigation of the effectiveness of indium for preventing the corrosion of cadmium alloy and lead first dealt with ingots cast from melts to which known amounts of indium had been added. Tests on specimens from such ingots indicated that, to obtain satisfactory resistance to corrosion in the presence of corroding lubricants, approximately 0.4 per cent of indium in the cadmium alloy, and approximately 4.0 per cent of indium in the lead, was desirable.

In the first attempts at electroplating indium and diffusing it into cadmium-alloy bearings, the assumption was made that the diffusion rate would be such that the indium could be concentrated in the surface layers; and, in accordance with this assumption, only enough indium to protect the surface layers was applied. These bearings, however, corroded badly when run with corrosive lubricant under engine operating conditions. It was only after a sufficient quantity of indium had been deposited on the surface of the bearings to provide for an average indium content of the bearing alloy near to the 0.4 per cent point that suitable corrosion resistance was obtained. Bearings into which this amount of indium had been diffused were sectioned and the complete depth of alloy exposed to corrosive media, with no resultant evidence of corrosion on the cut surfaces. (More detailed data along similar lines were presented in the paper to which the author

refers.) Results such as these very strongly indicate that the diffusion of indium was complete throughout the cadmium alloy and that to a considerable degree homogenization had taken place.

One possible explanation of the apparent difference in diffusion characteristics lies in the thicknesses of metal treated. The author's work was done on bars of 0.375-in. radius, which represents the thickness to which the indium would have had to diffuse before homogenization could begin. In contrast with this, the thickness of bearing metal of the bearings treated was on the order of 0.010 in. Assuming that the time required for total diffusion was some exponential function of the metal thickness, it should not be difficult to appreciate the variance that appears to occur between diffusion on thick and on thin metal. Another possible source of variance is in the amount of indium diffused—in contrast to 0.4 per cent average indium in diffused bearings, Fig. 2 shows an average indium content of approximately 6.5 per cent in the 0.020 thickness of cadmium alloy as checked by the author.

G. J. LEBRASSE,* Detroit, Mich.—The presentation of data relative to the diffusion of indium in bearings is of great practical importance at this time. The fact that the diffusion was greatest into the cadmium alloy is very interesting, because of the susceptibility of cadmium-base bearings to corrosion under certain operating conditions.

Our laboratory has obtained some interesting results on the diffusion of indium into several cadmium-silver alloys. The diffusion was accomplished at 350°F. for 2 hr. It was found that a good way to determine the effectiveness of diffusion was to section diffused bars diagonally and suspend them in an oil acidified with oleic acid, for several hours, at 325°F. These tests offered a quantitative means of determining the effectiveness of diffusion. It was found that minor impurities, as well as the major alloying constituents, had a marked effect on the depth of diffusion. Such data are of great importance in bearing applications where 0.020-in. diffusion is necessary to afford the

* Pontiac Motor Division, General Motors Corporation.

* Senior Metallurgist, Federal Mogul Corporation.

proper corrosion resistance after the bearings are line-reamed in place by the customer.

A. A. SMITH,* JR. (author's reply).—In studying diffusion, it does not make much difference how thick a sample is used, although it is preferable to have it thick enough so that zero concentration is reached before the specimen is completely machined. In diffusing indium into a bearing, it is very improbable that a homogeneous alloy is produced with the relatively short diffusion times that normally are used.

The data in the author's paper indicate that a large concentration gradient still exists even with the longest time of diffusion and it is likely that a similar gradient exists in a bearing liner. The method used by Mr. LeBrasse in determining the effectiveness of diffusion is of considerable practical importance, although it is doubtful whether the method would give quantitative values for rates of diffusion. The effect of various impurities in alloying elements on the rate of diffusion has been pointed out by a number of investigators and it is not surprising that these factors are important in the diffusion of indium into cadmium alloys.

Diffusion in Chromizing

By I. R. KRAMER,* MEMBER A.I.M.E.

(Chicago Meeting, October 1943)

[The final paper in the diffusion symposium was given by I. R. Kramer. The author called attention to the diffusion characteristics of chromium deposited on the surface of steel by treatment with chromium chloride and alloyed with the surface layer of the steel by thermal treatment. As the data cited were previously published in the paper "Chromizing of Steel," by I. R. Kramer and Robert H. Hafner (METALS TECHNOLOGY, October 1942, and in the TRANSACTIONS, volume 154, 1943, pages 415-420), it is unnecessary to reproduce these data here. The following paragraphs are taken from the author's presentation.—EDITOR.]

ASIDE from the well-known practical application of the diffusion phenomena to carburizing and calorizing, diffusion also finds application in adding alloying elements to the surfaces of steel parts. The chromizing of steels is a process by which the surface of a low-alloy steel may be enriched with chromium to form a highly corrosion-resistant case. This chromized case differs from an electroplated coat in that it is a diffused layer integral with the base metal and has all of the properties of a high-chromium steel.

Recently a method of chromizing has been developed in Germany by Daevs, Becker and Steinberg in which gaseous chromium chloride and hydrogen are passed over the steel at temperatures of 1650° to 1800°F. The chromium chloride reacts with the iron to give chromium and iron chloride. The chromium atoms are deposited on the surface and diffuse in as the iron atoms diffuse out, forming a layer rich in chromium. The principal role of hydrogen is to remove the carbon from the surface of the steel. Of the

two mechanisms, chemical reaction and diffusion, the one operating at the slower rate will determine the rate of formation of the layer. In this case, diffusion is slower and therefore any factors influencing its rate will affect the process.

The rate of diffusion is influenced by the temperature and crystal structure of the parent metal. Depth-concentration studies show that the concentration falls off gradually for a considerable distance and then drops sharply at about 13 per cent chromium, the point coincident with the boundary of the gamma loop.

The influence of the composition of the base metal upon diffusion is quite important. The depth of penetration of the chromium decreases as the carbon content increases and, of more importance, the chromized layer becomes brittle and is likely to spall if the carbon content is too high. It appears that in order to chromize successfully the carbon must be fixed by strong carbide-forming elements such as chromium or molybdenum, which decrease the diffusion of carbon. If this is not done, the carbon will diffuse from the interior faster than the chromium can diffuse inward, thus forming a carbide barrier.

The corrosion resistance of the chromized layer is high, and these steels offer some unique advantages over other corrosion-resisting coating or alloys. While chromizing is not meant to replace stainless steels, it may serve in the saving of alloying elements. The chromizing process uses soft or low alloyed steels that can be easily hot or cold formed and since the chromized layer is soft and firmly adherent, chromized parts can be subjected to cold deformation without spalling or chipping and without loss of corrosion resistance.

* Published by permission of the Navy Department.

* Metallurgist, Naval Research Laboratory, Washington, D. C.

Iron and Steel Division Volume 158, Transactions A.I.M.E., 1944

Howe Lecture

Gray Iron—Steel Plus Graphite. By J. T. MACKENZIE. (Metals Technology, June 1944)

Iron Ores and Blast Furnace Practice

Concentration of Iron Ores in the United States. By T. B. COUNSELMAN. (Metals Technology, December 1943)

Selection of Blast-furnace Refractories. By HOBART M. KRANER and E. B. SNYDER. (Metals Technology, April 1944)

The Washing of Pittsburgh Coking Coals and Results Obtained on Blast Furnaces. By C. D. KING. (Metals Technology, September 1943)

Steelmaking

The Role of Basic Slags in the Elimination of Phosphorus from Steel. By RICHARD L. BARRETT and WILLIAM J. McCAUGHEY. (Metals Technology, April 1944)

The Relative Deoxidizing Power of Boron in Liquid Steel and the Elimination of Boron in the Open-hearth Process. By R. W. GURRY. (Metals Technology, December 1943)

Manufacture and Properties of Killed Bessemer Steel. By E. C. WRIGHT. (Metals Technology, June 1944)

Hardenability

Effect of Sixteen Alloying Elements on Hardenability of Steel. By IRVIN R. KRAMER, ROBERT HAFNER and STEWART L. TOLEMAN. (Metals Technology, September 1943)

Effect of Quenching Temperature on the Results of the End-quench Hardenability Test. By CLARENCE E. JACKSON and ARTHUR L. CHRISTENSON. (Metals Technology, December 1943)

Effect of Some Elements on Hardenability. By WALTER CRAFTS and JOHN L. LAMONT. (Metals Technology, January 1944)

Effect of Several Variables on the Hardenability of High-carbon Steels. By E. S. ROWLAND, J. WELCHNER and R. H. MARSHALL. (Metals Technology, January 1944)

Mechanical Properties

Influence of Hydrogen on Mechanical Properties of Some Low-carbon Manganese-iron Alloys and on Hadfield Manganese Steel. By HERBERT H. UHLIG. (Metals Technology, June 1944)

Aging and the Yield Point in Steel. By J. R. LOW, JR., and M. GENSAMER. (Metals Technology, December 1943)

Tensile Properties of Medium-carbon Low-alloy Cast Steels. By H. A. SCHWARTZ and W. KENNETH BOCK. (Metals Technology, August 1944)

Variables Affecting the Results of Notched-bar Impact Tests on Steels. By CLARENCE E. JACKSON, MYRON A. PUGACZ and FRANK S. McKENNA. (Metals Technology, August 1944)

The Notched-bar Impact Test. By JOHN H. HOLLOMON. (Metals Technology, April 1944)

Hardness Measurement as a Rapid Means for Determining Carbon Content of Carbon and Low-alloy Steels. By K. L. CLARK and NICHOLAS KOWALL. (Metals Technology, January 1944)

Metallography

- Fracture and Comminution of Brittle Solids. (Abstract) By EUGENE F. PONCELET.
- Influence of Various Elements upon the Position of the Eutectoid in the Iron-carbon (Carbide) System. By CARL L. SHAPIRO and JEROME STRAUSS. (Metals Technology, December 1943)
- Orientation in Low-carbon Deep-drawing Steel. By JAMES K. STANLEY. (Metals Technology, September 1943)
- Recrystallization and Twin Relationships in Silicon Ferrite. By C. G. DUNN. (Metals Technology, February 1944)
- Precipitation and Reversion of Graphite in Low-carbon Low-alloy Steel in the Temperature Range 900° to 1300°F. By G. V. SMITH, R. F. MILLER and C. O. TARR. (Metals Technology, June 1944)
- The Bainite Reaction in Hypoeutectoid Steels. By E. P. Klier and TAYLOR LYMAN. (Metals Technology, June 1944)

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